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THE OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS IN THE VICINITY OF THE FREEZING POINT OF WATER.[1]

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To prepare for the measurement of osmotic pressure at low temperatures, an ice box of galvanized iron was suspended in each end of the bath which was described in a former paper.[2] The boxes consisted of superimposed and readily separated sections. The lowest of these extended from near the bottom of the tank to a short distance above the surface of the water, and they were held in their positions by means of lugs, riveted to the sides, which rested upon the top of the tank. They were provided with perforated bottoms. The sides were also perforated below the water line in order to insure a free circulation of water about the ice. The higher sections of the

[1] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The papers upon this subject which have preceded the present one will be found in THIS JOURNAL: **26**, 80; **28**, 1; **29**, 173; **32**, 93; **34**, 1; **36**, 1, 39; and **37**, 324.

[2] THIS JOURNAL, **36**, 1.

boxes were without bottoms, and served merely as lateral retainers for the ice. Each box extended upward in the air space to a height somewhat above the tops of the manometers, and each contained, when filled, about 75 kilograms of ice. Above the space between the boxes, and resting on their adjacent rims, was a galvanized iron tray, as wide as the tank, which was likewise filled with ice. Still further provision for cooling the air space above the water was made by placing a narrow ice box in the rear of the bath behind the manometers.

By means of the pumps, which were described in a former paper,[1] the water in the bath was kept in constant motion, and the air above it was made to circulate through the pipes lying in the water. To maintain a constant level, the surplus water, resulting from the melting of the ice, was continuously removed by means of a siphon with limbs of equal length and upturned ends. The horizontal portion of the siphon passed through one of the end walls of the bath, leaving one of the curved ends of the tube submerged in the water in the tank, and the other suspended over a waste pipe on the outside of the bath.

The extreme variations in the temperature of the water during the entire work were between 0°.12 and 0°.38, while the more frequent variations were between 0°.15 and 0°.30. The temperature of the air space above the water, in which the manometers were located, was always higher and much more variable. The difference, however, rarely exceeded 1°.0, except temporarily, after the opening of the bath. The generally higher and more fluctuating temperature of the air in the bath was due, of course, to the higher and rapidly changing temperature of the external air. The weather conditions under which the work was done were so unfavorable in these respects that the highest speed of the air pump did not suffice to maintain a constant relation between the temperature of the water and that of the air within the bath.

The material employed for the measurements was, as on former occasions, the purest obtainable "rock candy." It left no ash when burned, and gave no reaction for invert sugar

[1] This Journal, 36, 1.

with Fehling's solution. In this instance the usual determination of carbon and hydrogen was omitted, but not that with the polariscope. The standard solution[1] (containing 26.003 grams of sugar in 100 cc. at 17°.5) gave a rotation of 99.95, instead of 100, saccharimetric degrees.

The details of the individual measurements are presented in the following tables.

Tables I. to XXVII. give the record of the individual experiments in this (the III.) series of measurements of the osmotic pressure of cane sugar solutions. As in previous papers, no essential data have been omitted except the actual readings with the telescope. This is believed to be the proper course, because hereafter questions of interpretation will arise which cannot be adequately discussed unless all the essential quantitative facts pertaining to the measurements are within reach.

The results have been brought together, for convenience of examination, in Table XXVIII. and in Table XXIX. they have been summarized for each concentration of solution.

It will be noticed that every solution suffered some loss of rotation while in the cell, and that this loss has been interpreted and recorded in the tables (I. to XXVII.) as due to *inversion* of the cane sugar. It had been established on previous occasions[2] not only that inversion does always take place in the cell, but that such inversion exceeds that which occurs within the same time in identical solutions which are not enclosed in the osmotic cell.

We have been perfectly aware, however, that not all the loss of rotation is due to inversion, that in every case, in fact, a considerable portion of it results from a dilution of the solution in the cell which occurs while the cell is being closed at the beginning, and opened at the end, of an experiment, and also formerly, from a slipping of the manometer in the stopper or a crowding upwards of both manometer and stopper under the pressure of the cell contents, either of which movements increases the capacity of the cell and necessarily brings about

[1] Landolt, Das Optische Drehungsvermögen, p. 335.

[2] THIS JOURNAL, 34, 30; 36, 41.

Table I.

Original wt. normal concentration of solution, 0.1. Experiment No. 1
Rotation of original solution, 12°.5 (t = 22°). Manometer used, No. 18.
Rotation at conclusion of exp't, 12°.3 (t = 22°). Capillary depression, 0.02.
Loss in rotation, 0°.2 = 1.60 per cent. Cell used, B.
Calibration units of air in manometer, 476.96. Resistance of membrane, 137,500.
Time of setting up cell, 12.00 noon, Dec. 14, 1906. Initial pressure. 1.74 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						Difference between pressure found and calculated.
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	
Dec. 14.											
1.10 P.M.	0°.22	4°.1									
4.20 "	0°.18	0°.55									
8.00 "	0°.20	0°.52	159.50	159.20	1.01	0.43	0.03	0.02	2.41	2.23	+0.18
11.00 "	0°.18	0°.56	159.39	159.06	1.01	0.43	0.03	0.02	2.41	2.23	+0.18
Dec. 15.											
10.45 A.M.	0°.28	0°.65	159.37	158.99	1.00	0.43	0.03	0.02	2.42	2.23	+0.19
12.30 P.M.	0°.30	0°.84	159.40	158.90	1.00	0.43	0.03	0.02	2.42	2.23	+0.19
4.00 "	0°.36	0°.91	159.42	158.92	1.00	0.43	0.03	0.02	2.42	2.23	+0.19

Displacement of the manometer = 0.07 mm.

Table II.

Original wt. normal concentration of solution, 0.1. Experiment No. 2.
Rotation of original solution, 12°.5 (t = 20°). Manometer used, No. 18.
Rotation at conclusion of exp't, 12°.4 (t = 20°). Capillary depression, 0.02.
Loss in rotation, 0°.1 = 0.80 per cent. Cell used, B.
Calibration units of air in manometer, 476.96. Resistance of membrane, 136,000.
Time of setting up cell, 3.30 P. M., Dec. 17, 1906. Initial pressure, 2.09 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Dec. 17.											
5.00 P.M.	0°.23	3°.00									
7.30 "	0°.22	0°.80									
11.45 "	0°.14	0°.69	159.48	159.08	1.00	0.43	0.01	0.02	2.44	2.23	+0.21
Dec. 18.											
10.00 A.M.	0°.26	0°.59	158.71	158.37	1.01	0.43	0.01	0.02	2.44	2.23	+0.21
12.45 P.M.	0°.22	0°.56	158.66	158.33	1.01	0.43	0.01	0.02	2.44	2.23	+0.21
4.00 "	0°.22	0°.56	158.59	158.26	1.01	0.43	0.01	0.02	2.44	2.23	+0.21

Displacement of the manometer = 0.07 mm.

Table III.

Original wt. normal concentration of solution, 0.1. Experiment No. 3.
Rotation of original solution, 12°.65 (t = 18°.5). Manometer used No. 13.
Rotation at conclusion of exp't, 12°.60 (t = 18°.5). Capillary depression, 0.02.
Loss in rotation, 0°.05 = 0.39 per cent. Cell used, B.
Calibration units of air in manometer, 434.93. Resistance of membrane, 122,000.
Time of setting up cell, 3.30 P. M., Jan. 11, 1907. Initial pressure, 1.64 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Jan. 11.											
4.45 P.M.	0°.24	3°.00	205.93	205.12							
11.30 "	0°.14	0°.89	152.39	151.88	1.00	0.48	0.01	0.02	2.36	2.23	+0.13
Jan. 12.											
10.30 A.M.	0°.14	0°.95	152.08	151.55	1.00	0.48	0.01	0.02	2.36	2.23	+0.13
1.00 P.M.	0°.24	1°.12	152.15	151.52	0.99	0.48	0.01	0.02	2.37	2.23	+0.14
4.30 "	0°.24	1°.20	152.10	151.44	0.99	0.48	0.01	0.02	2.37	2.23	+0.14
7.30 "	0°.28	1°.30	152.11	151.39	1.00	0.48	0.01	0.02	2.36	2.23	+0.13
Jan. 13.											
10.15 "	0°.38	1°.17	151.11	150.46	1.01	0.48	0.01	0.02	2.37	2.23	+0.14

Displacement of the manometer = 0.09 mm.

Table IV.

Original wt. normal concentration of solution, 0.1. Experiment No. 4.
Rotation of original solution, 12°.65 (t = 18°.5). Manometer used, No. 6.
Rotation at conclusion of exp't, 12°.55 (t = 18°.5). Capillary depression, 0.02.
Loss in rotation, 0°.1 = 0.79 per cent. Cell used, A.
Calibration units of air in manometer, 396.89. Resistance of membrane, 157,000.
Time of setting up cell, 4.00 P. M., Jan. 11, 1907. Initial pressure, 1.34 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						Difference between pressure found and calculated.
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	
Jan. 11.											
4.45 P.M.	0°.24	3°.00	219.57								
11.30 "	0°.14	0°.89	160.90	160.38							
Jan. 12.											
10.30 A.M.	0°.14	0°.95	139.62	139.14	1.00	0.49	0.01	0.02	2.37	2.23	+0.14
1.00 P.M.	0°.24	1°.12	139.58	139.02	0.99	0.49	0.01	0.02	2.38	2.23	+0.15
4.30 "	0°.24	1°.20	139.43	138.82	0.99	0.49	0.01	0.02	2.39	2.23	+0.16
7.30 "	0°.28	1°.30	139.31	138.65	1.00	0.49	0.01	0.02	2.38	2.23	+0.15
Jan. 13.											
10.15 A.M.	0°.38	1°.17	138.58	137.99	1.01	0.49	0.01	0.02	2.39	2.23	+0.16

Displacement of the manometer = 0.09 mm.

Table V.

Original wt. normal concentration of solution, 0.2. Experiment No. 1.
Rotation of original solution, 24°.75 (t = 21°). Manometer used, No. 18.
Rotation at conclusion of exp't, 24°.60 (t = 21°). Capillary depression, 0.02.
Loss in rotation, 0°.15 = 0.61 per cent. Cell used, B.
Calibration units of air in manometer, 476.96. Resistance of membrane, 124,000.
Time of setting up cell, 4.00 P. M., Dec. 19, 1906. Initial pressure, 4.09 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Dec. 19.											
5.30 P.M.	0°.13	2°.30									
7.30 "	0°.14	0°.87									
11.00 "	0°.16	0°.69	91.35	91.12	1.01	0.52	0.02	0.02	4.74	4.46	+0.28
Dec. 20.											
10.00 A.M.	0°.20	0°.77	91.27	91.01	1.00	0.52	0.02	0.02	4.76	4.46	+0.30
12.45 P.M.	0°.24	0°.88	91.35	91.06	0.99	0.52	0.02	0.02	4.77	4.46	+0.31
3.30 "	0°.26	0°.91	91.32	91.02	0.99	0.52	0.02	0.02	4.77	4.46	+0.31

Displacement of the manometer = 0.05 mm.

Table VI.

Original wt. normal concentration of solution, 0.2. Experiment No. 2.
Rotation of original solution, 24°.8 (t = 21°). Manometer used, No. 18.
Rotation at conclusion of exp't, 24°.65 (t = 21°). Capillary depression, 0.02.
Loss in rotation, 0°.15 = 0.60 per cent. Cell used, B.
Calibration units of air in manometer, 476.96. Resistance of membrane, 122,000.
Time of setting up cell, 4.00 P. M., Dec. 21, 1906. Initial pressure, 3.79 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manom. eter.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Dec. 21.											
5.30 P.M.	0°.26	2°.40									
7.30 "	0°.28	1°.05									
10.00 "	0°.28	0°.99	91.90	91.57	0.99	0.52	0.02	0.02	4.74	4.46	+0.28
Dec. 22.											
9.30 A.M.	0°.28	0°.82	91.57	91.30	0.99	0.52	0.02	0.02	4.75	4.46	+0.29
1.00 P.M.	0°.32	0°.85	91.48	91.20	0.99	0.52	0.02	0.02	4.76	4.46	+0.30
5.00 "	0°.31	0°.95	91.49	91.17	0.99	0.52	0.02	0.02	4.76	4.46	+0.30

Displacement of the manometer = 0.05 mm.

Table VII.

Original wt. normal concentration of solution, 0.3. Experiment No. 1.
Rotation of original solution, 36°.6 (t = 22°). Manometer used, No. 21.
Rotation at conclusion of exp't, 36°.1 (t = 22°). Capillary depression, 0.02.
Loss in rotation, 0°.5 = 1.37 per cent. Cell used, B.
Calibration units of air in manometer, 471.37. Resistance of membrane, 158,000
Time of setting up cell, 4.00 P. M., Dec. 5, 1906. Initial pressure, 5.01 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manom-eter.	Uncor-rected.	Corrected.	Atmos-pheric pres-sure.	Liquids in manom-eter.	Inver-sion.	Capillary depres-sion.	Osmotic pressure cor-rected.	Theo-retical gas pres-sure.	Difference between pressure found and cal-culated.
Dec. 5.											
5.30 P.M.	0°.16	1°.93									
9.30 "	0°.14	0°.59									
Dec. 6.											
10.00 A.M.	0°.18	0°.70	63.30	63.14	0.99	0.58	0.07	0.02	7.01	6.68	+0.33
12.30 P.M.	0°.22	0°.89	63.27	63.07	0.98	0.58	0.07	0.02	7.02	6.68	+0.34
5.00 "	0°.30	1°.08	63.31	63.06	0.98	0.58	0.07	0.02	7.02	6.69	+0.33
10.30 "	0°.33	1°.00	63.33	63.10	0.99	0.58	0.07	0.02	7.01	6.69	+0.32
Dec. 7.											
10.00 A.M	0°.34	0°.70	63.12	62.96	1.00	0.58	0.07	0.02	7.02	6.69	+0.33
12.50 P.M.	0°.33	0°.74	63.14	62.97	1.00	0.58	0.07	0.02	7.02	6.69	+0.33
4.10 "	0°.34	0°.64	63.15	63.00	1.00	0.58	0.07	0.02	7.01	6.69	+0.32

Displacement of the manometer = 0.06 mm.

Table VIII.

Original wt. normal concentration of solution, 0.03. Experiment No. 2.
Rotation of original solution, 36°.6 (t = 20°). Manometer used, No. 18.
Rotation at conclusion of exp't, 36°.0 (t = 20°). Capillary depression, 0.02.
Loss in rotation, 0°.6 = 1.64 per cent. Cell used, B.
Calibration units of air in manometer, 476.96. Resistance of membrane, 122,000.
Time of setting up cell, 4.00 P. M., Dec. 11, 1906. Initial pressure, 5.79 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Dec. 11.											
5.30 P.M.	0°.16	1°.54									
9.15 "	0°.16	0°.44									
Dec. 12.											
12.10 A.M.	0°.15	0°.36	63.43	63.34	1.01	0.56	0.08	0.02	7.02	6.68	+0.34
10.00 "	0°.14	0°.29	63.35	63.28	1.02	0.56	0.08	0.02	7.02	6.68	+0.34
12.50 P.M.	0°.14	0°.37	63.35	63.27	1.01	0.56	0.08	0.02	7.03	6.68	+0.35
3.50 "	0°.18	0°.53	63.36	63.24	1.01	0.56	0.08	0.02	7.03	6.68	+0.35

Displacement of the manometer = 0.06 mm.

Table IX.

Original wt. normal concentration of solution, 0.4. Experiment No. 1.
Rotation of original solution, 47°.85 (t = 22°). Manometer used, No. 13.
Rotation at conclusion of exp't, 47°.30 (t = 22). Capillary depression, 0.02.
Loss in rotation, 0°.55 = 1.15 per cent. Cell used, B.
Calibration units of air in manometer, 434.93. Resistance of membrane, 140,000.
Time of setting up cell, 4.00 P. M., Dec. 26, 1906. Initial pressure, 7.73 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Dec. 26.											
5.00 P.M.	0°.18	3°.30	54.32								
8.00 "	0°.16	0°.75	45.32								
11.00 "	0°.16	0°.63	44.88	44.78	1.00	0.62	0.08	0.02	9.27	8.91	+0.36
Dec. 27.											
9.45 A.M.	0°.16	0°.57	44.78	44.69	1.00	0.62	0.08	0.02	9.29	8.91	+0.38
12.30 P.M.	0°.20	0°.71	44.80	44.69	1.00	0.62	0.08	0.02	9.29	8.91	+0.38
4.00 "	0°.22	0°.79	44.79	44.66	0.99	0.62	0.08	0.02	9.31	8.91	+0.40

Displacement of the manometer = 0.08 mm.

Table X.

Original wt. normal concentration of solution, 0.4. Experiment No. 2.
Rotation of original solution, 48°.0 (t = 20°). Manometer used, No. 6.
Rotation at conclusion of exp't, 47°.4 (t = 20°). Capillary depression, 0.02.
Loss in rotation, 0°.6 (1.25 per cent). Cell used, B.
Calibration units of air in manometer, 396.89. Resistance of membrane, 124,444.
Time of setting up cell, 4.00 P. M., Dec. 28, 1906. Initial pressure, 6.60 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Dec. 28.											
5.00 P.M.	0°.22	3°.5	57.85								
7.30 "	0°.23	1°.07									
11.15 "	0°.22	1°.04	41.24	41.08	1.00	0.65	0.08	0.02	9.25	8.91	+0.34
Dec. 29.											
9.15 A.M.	0°.26	1°.03	41.24	41.08	1.00	0.65	0.08	0.02	9.25	8.92	+0.33
1.00 P.M.	0°.33	1°.17	41.22	41.04	1.00	0.65	0.08	0.02	9.26	8.92	+0.34
4.00 "	0°.32	1°.26	41.23	41.04	1.00	0.65	0.08	0.02	9.26	8.92	+0.34

Displacement of the manometer = 0.07 mm.

Table XI.

Original wt. normal concentration of solution, 0.4.
Rotation of original solution, 48°.0 (t = 20°).
Rotation at conclusion of exp't, 47°.6 (t = 20°).
Loss in rotation, 0°.4 = 0.83 per cent.
Calibration units of air in manometer, 434.98.
Time of setting up cell, 3.30 P. M., Jan. 5, 1907.

Experiment No. 3.
Manometer used, No. 5.
Capillary depression, 0.02.
Cell used, B.
Resistance of membrane, 136,600.
Initial pressure, 7.57 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Jan. 5.											
5.15 P.M.	0°.26	3°.00	55.49								
8.00 "	0°.18	1°.18	45.56								
12.00 "	0°.20	0°.97	45.23								
Jan. 6.											
10.00 A.M.	0°.22	0°.85	45.21								
2.45 P.M.	0°.24	0°.96	45.21								
7.30 "	0°.26	1°.01	45.04	44.87	1.00	0.63	0.06	0.02	9.28	8.92	+0.36
Jan. 7.											
10.15 A.M.	0°.32	1°.17	45.00	44.81	1.01	0.63	0.06	0.02	9.29	8.92	+0.37
12.30 P.M.	0°.34	1°.39	44.99	44.76	1.00	0.63	0.06	0.02	9.31	8.92	+0.39
3.45 "	0°.34	1°.54	45.01	44.75	1.00	0.63	0.06	0.02	9.31	8.92	+0.39

Displacement of the manometer = 0.22 mm.

Table XII.

Original wt. normal concentration of solution, 0.4.
Rotation of original solution, 48°.0 (t = 20°.5).
Rotation at conclusion of exp't, 47°.6 (t = 20°.5).
Loss in rotation, 0.4 = 0.83 per cent.
Calibration units of air in manometer, 396.89.
Time of setting up cell, 4.00 P. M., Jan. 9, 1907.

Experiment No. 4.
Manometer used, No. 6.
Capillary depression, 0.02.
Cell used, D.
Resistance of membrane, 93,000.
Initial pressure, 8.08 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Jan. 9.											
5.30 P.M.	0°.22	3°.30	47.68								
7.30 "	0°.16	0°.89	41.51	41.37							
10.30 "	0°.14	0°.77	41.28	41.16	1.00	0.65	0.06	0.02	9.25	8.91	+0.34
Jan. 10.											
10.00 A.M.	0°.16	0°.64	41.27	41.17	1.00	0.65	0.06	0.02	9.25	8.91	+0.34
1.00 P.M.	0°.16	0°.72	41.28	41.17	1.00	0.65	0.06	0.02	9.25	8.91	+0.34
4.00 "	0°.12	0°.81	41.28	41.16	0.99	0.65	0.06	0.02	9.26	8.91	+0.35

Displacement of the manometer = 0.04 mm.

Table XIII.

Original wt. normal concentration of solution, 0.5. Experiment No. 1.
Rotation of original solution, 58°.7 (t = 19°.5). Manometer used, No. 21.
Rotation at conclusion of exp't, 57°.8 (t = 19°.5). Capillary depression, 0.02.
Loss in rotation, 0°.9 = 1.53 per cent. Cell used, G.
Calibration units of air in manometer, 471.37. Resistance of membrane, 58,947.
Time of setting up cell, 5.00 P. M., Nov. 26, 1906. Initial pressure, 11.03 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						Difference between pressure found and calculated.
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	
Nov. 26.											
7.30 P.M.	0°.24	1°.88									
11.10 "	0°.26	1°.69									
Nov. 27.											
10.10 A.M.	0°.33	1°.80	39.46	39.20	1.00	0.61	0.13	0.02	11.53	11.14	+0.39
12.40 P.M.	0°.38	1°.99	39.50	39.21	1.00	0.61	0.13	0.02	11.52	11.15	+0.37
3.30 "	0°.38	2°.03	39.48	39.19	1.00	0.61	0.13	0.02	11.53	11.15	+0.38
7.30 "	0°.16	1°.29	39.36	39.18	1.01	0.61	0.13	0.02	11.52	11.14	+0.38
11.15 "	0°.14	1°.20	39.28	39.11	1.00	0.61	0.13	0.02	11.56	11.14	+0.42
Nov. 28.											
10.00 A.M.	0°.18	1°.33	39.36	39.17	1.00	0.61	0.13	0.02	11.54	11.14	+0.40

Displacement of the manometer = 0.24 mm.

Table XIV.

Original wt. normal concentration of solution, 0.5. Experiment No. 2.
Rotation of original solution, 58°.75 (t = 18°.5). Manometer used, No. 21.
Rotation at conclusion of exp't, 57°.75 (t = 18°.5). Capillary depression, 0.02.
Loss in rotation, 1°.00 = 1.70 per cent. Cell used, G.
Calibration units of air in manomter, 471.37. Resistance of membrane, 135,000.
Time of setting up cell, 12.30 P. M., Nov. 30, 1906. Initial pressure, 11.39 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Nov. 30.											
3.30 P.M.	0°.22	0°.77									
7.30 "	0°.20	0°.69									
11.00 "	0°.20	0°.69	39.19	39.09	1.00	0.61	0.14	0.02	11.55	11.14	+0.41
Dec. 1.											
9.15 A. M.	0°.26	0°.76	39.05	38.94	1.00	0.61	0.14	0.02	11.60	11.14	+0.46
12.40 P.M.	0°.22	0°.81	39.03	38.91	1.00	0.61	0.14	0.02	11.61	11.14	+0.47
4.00 "	0°.22	0°.79	39.04	38.93	1.00	0.61	0.14	0.02	11.60	11.14	+0.46

Displacement of the manometer = 0.22.

Table XV.

Original wt. normal concentration of solution, 0.5. Experiment No. 3.
Rotation of original solution, 58°.80 (t = 20°). Manometer used, No. 18.
Rotation at conclusion of exp't, 57°.75 (t = 20°). Capillary depression, 0.02.
Loss in rotation, 1°.05 = 1.71 per cent. Cell used, G.
Calibration units of air in manometer, 476.96. Resistance of membrane, 110,000.
Time of setting up cell, 3.30 P. M., Dec. 3, 1906. Initial pressure, 11.30 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Dec. 3											
5.20 P.M.	0°.16	5°.00									
7.45 "	0°.16	0°.66									
11.15 "	0°.14	0°.39									
Dec. 4											
10.20 A.M.	0°.12	0°.20	39.10	39.07	1.01	0.59	0.15	0.02	11.65	11.14	+0.51
12.45 P.M.	0°.12	0°.25	39.13	39.09	1.01	0.59	0.15	0.02	11.65	11.14	+0.51
3.45 "	0°.12	0°.33	39.17	39.12	1.01	0.59	0.15	0.02	11.64	11.14	+0.50
7.45 "	0°.14	0°.39	39.17	39.11	1.00	0.59	0.15	0.02	11.65	11.14	+0.51
11.00 "	0°.15	0°.40	39.16	39.10	1.01	0.59	0.15	0.02	11.64	11.14	+0.50
Dec. 5											
10.10 A.M.	0°.18	0°.38	39.15	39.09	1.01	0.59	0.15	0.02	11.65	11.14	+0.51
4.15 P.M.	0°.18	0°.52	39.18	39.11	1.00	0.59	0.15	0.02	11.65	11.14	+0.51

Displacement of the manometer = 0.07.

Table XVI.

Original wt. normal concentration of solution, 0.5. Experiment No. 4.
Rotation of original solution, 58°.85 (t = 20°). Manometer used, No. 11.
Rotation at conclusion of exp't, 58°.10 (t = 20°). Capillary depression, 0.02.
Loss in rotation, 0°.75 = 1.29 per cent. Cell used, D.
Calibration units of air in manometer, 465.78. Resistance of membrane, 90,000.
Time of setting up cell, 4.30 P. M., Jan. 4, 1907. Initial pressure, 8.13 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Jan. 4											
5.15 P.M.	0°.26	2°.10	54.70								
8.00 "	0°.16	1°.07	38.70								
10.45 "	0°.16	0°.97	38.31	38.17	1.00	0.56	0.11	0.02	11.67	11.14	+0.53
Jan. 5											
10.30 A.M.	0°.18	0°.89	38.24	38.12	1.01	0.56	0.11	0.02	11.68	11.14	+0.54
1.00 P.M.	0°.20	1°.09	38.28	38.13	1.00	0.56	0.11	0.02	11.69	11.14	+0.55
4.00 "	0°.26	1°.26	38.31	38.12	1.00	0.56	0.11	0.02	11.69	11.14	+0.55

Displacement of the manometer = 0.38 mm.

Table XVII.

Original wt. normal concentration of solution, 0.6. Experiment No. 1.
Rotation of original solution, 69°.4 (t = 19°). Manometer used, No. 13.
Rotation at conclusion of exp't, 68°.2 (t = 19°). Capillary depression, 0.02.
Loss in rotation, 1°.2 = 1.73 per cent. Cell used, B.
Calibration units of air in manometer, 434.93. Resistance of membrane, 161,000.
Time of setting up cell, 4.30 P. M., Dec. 31, 1906. Initial pressure, 12.08.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Dec. 31.											
6.00 P.M.	0°.22	2°.00	35.26								
11.00 "	0°.16	1°.34	30.19	30.04	1.00	0.64	0.12	0.02	14.02	13.37	+0.65
Jan. 1, '07											
10.00 A.M.	0°.22	1°.20	30.19	30.06	1.00	0.64	0.12	0.02	14.01	13.37	+0.64
12.30 P.M.	0°.22	1°.29	30.19	30.05	1.00	0.64	0.12	0.02	14.01	13.37	+0.64
5.30 "	0°.24	1°.28	30.21	30.07	1.01	0.64	0.12	0.02	13.99	13.37	+0.62
7.30 "	0°.28	1°.43	30.24	30.08	1.01	0.64	0.12	0.02	13.99	13.37	+0.62
11.00 "	0°.25	1°.36	30.24	30.09	1.01	0.64	0.12	0.02	13.98	13.37	+0.61
Jan. 2, '07											
9,30 A.M.	0°.24	1°.10	30.18	30.06	1.01	0.64	0.12	0.02	14.00	13.37	+0.63

Displacement of the manometer = 0.48 mm.

Table XVIII.

Original wt. normal concentration of solution, 0.6.
Rotation of original solution, 69°.35 (t = 20°).
Rotation at conclusion of exp't, 68°.05 (t = 20°).
Loss in rotation, 1°.30 = 1.86 per cent.
Calibration units of air in manometer, 369.89.
Time of setting up cell, 4.00 P. M., Jan. 2, 1907.
Experiment No. 2.
Manometer used, No. 6.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 102,000.
Initial pressure, 13.09.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Jan. 2.											
5.00 P.M.	0°.24	3°.3	29.97								
8.00 "	0°.20	1°.01	27.63	27.53	1.01	0.67	0.14	0.02	13.96	13.37	+0.59
10.30 "	0°.20	0°.94	27.60	27.51	1.01	0.67	0.14	0.02	13.97	13.37	+0.60
Jan. 3											
10.15 A.M.	0°.20	0°.84	27.63	27.55	1.01	0.67	0.14	0.02	13.95	13.37	+0.58
1.00 P.M.	0°.22	0°.92	27.60	27.51	1.01	0.67	0.14	0.02	13.97	13.37	+0.60
4.15 "	0°.25	0°.95	27.59	27.49	1.01	0.67	0.14	0.02	13.98	13.37	+0.61

Displacement of the manometer = 0.10 mm.

Table XIX.

Original wt. normal concentration of solution, 0.7. Experiment No. 1.
Rotation of original solution, 79°.3 (t = 20°). Manometer used, No. 13.
Rotation at conclusion of exp't, 78°.1 (t = 20°). Capillary depression, 0.02.
Loss in rotation, 1°.2 = 1.51 per cent. Cell used, B.
Calibration units of air in manometer, 434.93. Resistance of membrane, 159,300.
Time of setting up cell, 4.00 P.M., Jan. 3, 1907. Initial pressure, 13.53.

	Temperature.		Volume of air in manometer.		Corrections.						Difference between pressure found and calculated.
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	
Jan. 3.											
5.15 P.M.	0°.18	2°.80	31.68								
8.15 "	0°.16	0°.91	25.85								
10.45 "	0°.16	0°.93	25.74	25.65	1.00	0.65	0.18	0.02	16.45	15.60	+0.85
Jan. 4											
10.00 A.M.	0°.26	1°.29	25.73	25.61	0.99	0.65	0.18	0.02	16.48	15.60	+0.88
12.45 P.M.	0°.30	1°.38	25.75	25.62	0.99	0.65	0.18	0.02	16.48	15.60	+0.88
4.15 "	0°.32	1°.19	25.74	25.64	1.00	0.65	0.18	0.02	16.46	15.60	+0.86

Displacement of the manometer = 0.61 mm.

Table XX.

Original wt. normal concentration of solution, 0.7. Experiment No. 2.
Rotation of original solution, 79°.3 (t = 20°). Manometer used, No. 6.
Rotation at conclusion of exp't, 78°.2 (t = 20°). Capillary depression, 0.02.
Loss in rotation, 1°.1 = 1.39 per cent. Cell used, D.
Calibration units of air in manometer, 396.89. Resistance of membrane, 111,500.
Time of setting up cell, 1.30 P. M., Jan. 18, 1907. Initial pressure, 13.84 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Jan. 18											
1.15 P.M.	0°.16	4°.5	28.51								
5.15 "	0°.14	0°.59	23.37	23.32	1.00	0.67	0.16	0.02	16.55	15.60	+0.95
7.30 "	0°.16	0°.83	23.40	23.33	1.00	0.67	0.16	0.02	16.54	15.60	+0.94
11.45 "	0°.14	0°.76	23.37	23.31	1.00	0.67	0.16	0.02	16.56	15.60	+0.96
Jan. 19											
10.30 A.M.	0°.16	0°.71	23.41	23.35	1.00	0.67	0.16	0.02	16.53	15.60	+0.93

Displacement of the manometer = 0.45 mm.

Table XXI.

Original wt. normal concentration of solution, 0.8. Experiment No. 1.
Rotation of original solution, 89°.15 (t = 20°). Manometer used, No. 6.
Rotation at conclusion of exp't, 87°.60 (t = 20°). Capillary depression, 0.02.
Loss in rotation, 1°.55 = 1.74 per cent. Cell used, G.
Calibration units of air in manometer, 396.89. Resistance of membrane, 112,000.
Time of setting up cell, 4.00 P. M., Jan. 4, 1907. Initial pressure, 17.64 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Jan. 4											
5.15 P.M.	0°.26	2°.10	22.28								
8.00 "	0°.16	1°.07	20.54								
10.45 "	0°.16	0°.97	20.43	20.36	1.00	0.68	0.23	0.02	18.96	17.82	+1.14
Jan. 5											
10.30 A.M.	0°.18	0°.89	20.46	20.39	1.01	0.68	0.23	0.02	18.92	17.82	+1.01
1.00 P.M.	0°.20	1°.09	20.49	20.41	1.00	0.68	0.23	0.02	18.92	17.82	+1.10
4.00 "	0°.26	1°.26	20.50	20.41	1.00	0.68	0.23	0.02	18.92	17.83	+1.09

Displacement of the manometer = 0.01 mm.

Table XXII.

Original wt. normal concentration of solution, 0.8. Experiment No. 2.
Rotation of original solution, 89°.0 (t = 20°.5). Manometer used, No. 6.
Rotation at conclusion of exp't, 87°.4 (t = 20°.5). Capillary depression, 0.02.
Loss in rotation, 1°.6 = 1.80 per cent. Cell used, G.
Calibration units of air in manometer, 396.89. Resistance of membrane, 110,000.
Time of setting up cell, 4.15 P. M., Jan. 14, 1907. Initial pressure, 17.68 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Jan. 14.											
6.00 P.M.	0°.22	2°.60	22.27								
7.30 "	0°.16	1°.19	20.60	20.51	1.00	0.67					
11.00 "	0°.16	1°.00	20.47	20.40	1.00	0.67	0.24	0.02	18.91	17.82	+1.09
Jan. 15											
10.15 A.M.	0°.22	0°.96	20.49	20.42	1.00	0.67	0.24	0.02	18.89	17.82	+1.07
1.00 P.M.	0°.26	1°.06	20.48	20.40	1.00	0.67	0.24	0.02	18.91	17.83	+1.08
5.00 "	0°.26	1°.06	20.48	20.40	1.00	0.67	0.24	0.02	18.91	17.83	+1.08
8.00 "	0°.26	0°.96	20.49	20.42	1.01	0.67	0.24	0.02	18.88	17.83	+1.05
11.30 "	0°.26	0°.91	20.46	20.39	1.01	0.67	0.24	0.02	18.90	17.83	+1.07
Jan. 16											
10.15 A.M.	0°.26	0°.69	20.47	20.42	1.01	0.67	0.24	0.02	18.88	17.83	+1.05
1.00 P.M.	0°.26	0°.80	20.48	20.42	1.01	0.67	0.24	0.02	18.88	17.83	+1.05
3.30 "	0°.26	0°.80	20.47	20.41	1.01	0.67	0.24	0.02	18.89	17.83	+1.06

Displacement of the manometer = 0.34 mm.

Table XXIII.

Original wt. normal concentration of solution, 0.9. Experiment No. 1.
Rotation of original solution, 98°.30 (t = 21°). Manometer used, No. 13.
Rotation at conclusion of exp't, 96°.45 (t = 21°). Capillary depression, 0.02.
Loss in rotation, 1°.85 = 1.88 per cent. Cell used, G.
Calibration units of air in manometer, 434.93. Resistance of membrane, 101,000.
Time of setting up cell, 3.30 P. M., Dec. 20, 1906. Initial pressure, 20.05 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Dec. 20											
4.45 P.M.	0°.22	2°.50									
7.30 "	0°.26	0°.94									
Dec. 21											
12.30 A.M.	0°.31	0°.83	19.63	19.57	0.99	0.66	0.29	0.02	21.62	20.06	+1.56
10.00 "	0°.30	0°.84	19.62	19.56	0.99	0.66	0.29	0.02	21.64	20.06	+1.58
12.30 P.M.	0°.32	0°.99	19.63	19.56	0.99	0.66	0.29	0.02	21.64	20.06	+1.58
4.15 "	0°.33	1°.05	19.64	19.56	0.99	0.66	0.29	0.02	21.64	20.06	+1.58

Displacement of the manometer = 0.44 mm.

Table XXIV.

Original wt. normal concentration of solution, 0.9. Experiment No. 2.
Rotation of original solution, 98°.40 (t = 18°.5). Manometer used, No. 13.
Rotation at conclusion of exp't, 96°.45 (t = 18°.5). Capillary depression, 0.02.
Loss in rotation, 1°.95 = 1.98 per cent. Cell used, G.
Calibration units of air in manometer, 434.93. Resistance of membrane, 102,000.
Time of setting up cell, 3.30 P.M., Dec. 29, 1906. Initial pressure, 20.66 atmospheres.

Time.	Temperature.		Volume of air in manometer.		Corrections.				Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.			
Dec. 29											
5.30 P.M.	0°.22	1°.80	20.87								
8.00 "	0°.16	1°.06	19.75								
11.30 "	0°.15	0°.97	19.65	19.58	1.01	0.66	0.30	0.02	21.58	20.05	+1.53
Dec. 30											
10.00 A.M.	0°.22	1°.04	19.68	19.61	1.01	0.66	0.30	0.02	21.55	20.05	+1.50
1.00 P.M.	0°.22	1°.13	19.68	19.60	1.00	0.66	0.30	0.02	21.56	20.05	+1.51
5.00 "	0°.25	1°.19	19.69	19.60	1.00	0.66	0.30	0.02	21.56	20.05	+1.51

Displacement of the manometer = 0.05 mm.

Table XXV.

Original wt. normal concentration of solution, 1.0. Experiment No. 1.
Rotation of original solution, 107°.2 (t = 23°). Manometer used, No. 21.
Rotation at conclusion of exp't, 104°.3 (t = 23°). Capillary depression, 0.02.
Loss in rotation, 2°.9 = 2.71 per cent. Cell used, G.
Calibration units of air in manometer, 471.37. Resistance of membrane, 90,000.
Time of setting up cell, 3.30 P.M., Dec. 12, 1906. Initial pressure, 23.00 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manometer.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Dec. 12											
5.00 P.M.	0°.14	2°.3									
7.30 "	0°.13	0°.52									
11.10 "	0°.12	0°.44									
Dec. 13											
10.15 A.M.	0°.16	0°.44	18.98	18.95	1.00	0.64	0.46	0.02	24.07	22.28	+1.79
12.30 P.M.	0°.18	0°.59	19.00	18.96	1.00	0.64	0.46	0.02	24.06	22.28	+1.79
4.10 "	0°.18	0°.68	18.99	18.94	1.00	0.64	0.46	0.02	24.09	22.28	+1.81
8.00 "	0°.20	0°.72	19.02	18.97	1.00	0.64	0.46	0.02	24.05	22.28	+1.77
11.15 "	0°.24	0°.75	19.01	18.96	1.00	0.64	0.46	0.02	24.06	22.28	+1.78
Dec. 14											
10.00 A.M.	0°.26	0°.70	19.00	18.95	1.01	0.64	0.46	0.02	24.06	22.29	+1.77
12.30 P.M.	0°.30	0°.72	18.99	18.94	1.01	0.64	0.46	0.02	24.08	22.29	+1.79

Displacement of the manometer = 0.23 mm.

Table XXVI.

Original wt. normal concentration of solution, 1.0.
Rotation of original solution, 107.3 (t = 21°.5).
Rotation at conclusion of exp't, 103°.8 (t = 21°.5).
Loss in rotation, 3°.5 = 3.26 per cent.
Calibration units of air in manometer, 465.78.
Time of setting up cell, 5.30 P. M., Dec. 15, 1906.

Experiment No. 2.
Manometer used, No. 11.
Capillary depression, 0.02.
Cell used, G.
Resistance of membrane, 128,000.
Initial pressure, 24.35 atmospheres.

Time.	Temperature. Solution.	Temperature. Air in manom-eter.	Volume of air in manometer. Uncorrected.	Volume of air in manometer. Corrected.	Corrections. Atmospheric pressure.	Corrections. Liquids in manometer.	Corrections. Inversion.	Corrections. Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Dec. 15											
6.30 P.M.	0°.24	2°.80									
11.30 "	0°.20	1°.00	18.76	18.69	1.00	0.58	0.56	0.02	23.96	22.28	+1.68
Dec. 16											
9.45 A.M.	0°.24	0°.82	18.75	18.69	1.00	0.58	0.56	0.02	23.96	22.28	+1.68
1.00 P.M.	0°.24	0°.83	18.73	18.67	1.00	0.58	0.56	0.02	23.99	22.28	+1.71
6.30 "	0°.24	0°.80	18.73	18.68	1.00	0.58	0.56	0.02	23.97	22.28	+1.69
10.30 "	0°.25	0°.80	18.74	18.68	1.00	0.58	0.56	0.02	23.97	22.28	+1.69
Dec. 17											
10.15 A.M.	0°.25	0°.85	18.73	18.67	1.00	0.58	0.56	0.02	23.99	22.28	+1.71
1.00 P.M.	0°.30	0°.97	18.74	18.67	1.00	0.58	0.56	0.02	23.99	22.29	+1.70
4.00 "	0°.34	0°.96	18.73	18.66	1.00	0.58	0.56	0.02	24.00	22.29	+1.71

Displacement of the manometer = 0.59 mm.

Table XXVII.

Original wt. normal concentration of solution, 1.0.
Rotation of original solution, 107°.2 (t = 20°.5).
Rotation at conclusion of exp't, 105°.2 (t = 20°.5).
Loss in rotation, 2°.0 = 1.87 per cent.
Calibration units of air in manometer, 434.93.
Time of setting up cell, 4.30 P. M., Jan. 14, 1907.
Experiment No. 3.
Manometer used, No. 13.
Capillary depression, 0.02.
Cell used, A.
Resistance of membrane, 134,000.
Initial pressure, 16.13 atmospheres.

	Temperature.		Volume of air in manometer.		Corrections.						
Time.	Solution.	Air in manometer.	Uncorrected.	Corrected.	Atmospheric pressure.	Liquids in manometer.	Inversion.	Capillary depression.	Osmotic pressure corrected.	Theoretical gas pressure.	Difference between pressure found and calculated.
Jan. 14.											
6.00 P.M.	0°.22	2°.60	26.67								
7.30 "	0°.16	1°.19	21.44	21.35							
11.00 "	0°.16	1°.00	19.27	19.20							
Jan. 15											
10.15 A.M.	0°.22	0°.96	17.80	17.74							
1.00 P.M.	0°.26	1°.06	17.80	17.73							
5.00 "	0°.26	1°.06	17.78	17.71							
8.00 "	0°.26	0°.96	17.75	17.69	1.01	0.65	0.31	0.02	23.95	22.29	+1.66
11.30 "	0°.26	0°.91	17.72	17.66	1.01	0.65	0.31	0.02	23.99	22.29	+1.70
Jan. 16											
10.30 A.M.	0°.26	0°.69	17.73	17.69	1.01	0.65	0.31	0.02	23.95	22.29	+1.66
1.00 P.M.	0°.26	0°.80	17.73	17.68	1.01	0.65	0.31	0.02	23.96	22.29	+1.67
3.30 "	0°.26	0°.80	17.73	17.68	1.01	0.65	0.31	0.02	23.96	22.29	+1.67

Displacement of the manometer = 0.91 mm.

Table XXVIII.—The Osmotic Pressure of Cane Sugar Solutions in the Vicinity of o°.

Series III.

Weight normal concentration.	No. of experiment.	Temperature of solution.			Osmotic pressure observed (atmospheres).			Calculated gas pressure for same temperature.	Difference b'tw'n mean osmotic and mean gas pressure.	Ratio of osmotic to gas pressure.
		Mean.	Highest.	Lowest.	Mean.	Highest.	Lowest.	Atmospheres.		
0.1	1	0°.26	0°.36	0°.18	2.42	2.42	2.41	2.23	0.19	1.085
"	2	0°.21	0°.26	0°.14	2.44	2.44	2.44	2.23	0.21	1.094
"	3	0°.24	0°.38	0°.14	2.37	2.37	2.36	2.23	0.14	1.063
"	4	0°.24	0°.38	0°.14	2.38	2.39	2.37	2.23	0.15	1.067
0.2	1	0°.22	0°.26	0°.16	4.76	4.77	4.74	4.46	0.30	1.067
"	2	0°.30	0°.32	0°.28	4.75	4.76	4.74	4.46	0.29	1.065
0.3	1	0°.29	0°.34	0°.18	7.02	7.02	7.01	6.69	0.33	1.049
"	2	0°.15	0°.18	0°.14	7.03	7.03	7.02	6.68	0.35	1.052
0.4	1	0°.19	0°.22	0°.16	9.29	9.31	9.27	8.91	0.38	1.043
"	2	0°.28	0°.33	0°.22	9.26	9.26	9.25	8.92	0.34	1.038
"	3	0°.32	0°.34	0°.26	9.30	9.31	9.28	8.92	0.38	1.043
"	4	0°.15	0°.16	0°.12	9.25	9.26	9.25	8.91	0.34	1.038
0.5	1	0°.26	0°.38	0°.14	11.53	11.56	11.52	11.14	0.39	1.035
"	2	0°.23	0°.26	0°.20	11.59	11.61	11.55	11.14	0.45	1.040
"	3	0°.14	0°.18	0°.12	11.65	11.65	11.64	11.14	0.51	1.046
"	4	0°.20	0°.26	0°.16	11.68	11.69	11.67	11.14	0.54	1.048
0.6	1	0°.23	0°.28	0°.16	14.00	14.02	13.98	13.37	0.63	1.047
"	2	0°.21	0°.25	0°.20	13.97	13.98	13.95	13.37	0.60	1.045
0.7	1	0°.26	0°.32	0°.16	16.47	16.48	16.45	15.60	0.87	1.056
"	2	0°.15	0°.16	0°.14	16.55	16.56	16.53	15.60	0.95	1.061
0.8	1	0°.20	0°.26	0°.16	18.93	18.96	18.92	17.82	1.11	1.062
"	2	0°.24	0°.26	0°.16	18.89	18.91	18.88	17.83	1.06	1.059
0.9	1	0°.32	0°.33	0°.30	21.64	21.64	21.62	20.06	1.58	1.079
"	2	0°.21	0°.25	0°.15	21.56	21.58	21.55	20.05	1.51	1.075
1.0	1	0°.22	0°.30	0°.16	24.07	24.09	24.05	22.28	1.79	1.080
"	2	0°.26	0°.34	0°.20	23.98	24.00	23.96	22.28	1.70	1.076
"	3	0°.26	0°.26	0°.26	23.96	23.99	23.95	22.29	1.67	1.075

a dilution of the solution within. The question of dilution and of the distribution, in the correction of results, of loss in rotation between dilution and inversion has been referred to frequently in former papers,[1] and it must continue to be a matter of great concern to us until, through improvements in cells and manipulation, we have succeeded in suppressing dilution or in reducing it to harmless proportions.

Table XXIX.—The Osmotic Pressure of Cane Sugar Solutions in the Vicinity of 0°. Mean Values for Each Concentration.

Series III

Weight-normal concentration.	Temperature.	Observed osmotic pressure. Atmospheres.	Calculated gas pressure. Atmospheres.	Difference between osmotic and gas pressures. Atmospheres.	Ratio of osmotic to gas pressure.
0.1	0°.24	2.40	2.23	0.17	1.077
0.2	0°.26	4.76	4.46	0.30	1.067
0.3	0°.22	7.03	6.69	0.34	1.051
0.4	0°.24	9.28	8.92	0.36	1.040
0.5	0°.21	11.61	11.14	0.47	1.042
0.6	0°.22	13.99	13.37	0.62	1.046
0.7	0°.21	16.51	15.60	0.91	1.058
0.8	0°.22	18.99	17.83	1.08	1.060
0.9	0°.27	21.60	20.06	1.54	1.077
1.0	0°.25	24.00	22.28	1.72	1.077

We have stated[2] that the dilution which occurs in our cells is not due to leakage of the solutions through the membranes. The evidence of this upon which we principally rely at the present time is the demonstrated ability of the membranes to sustain for long periods, undiminished, the maximum pressures which the solutions have, under any circumstances, been found to exert. Solutions in cells with leaky membranes may, and often do, exhibit *constant* pressures for considerable periods, but such pressures are lower than those obtained under the

[1] THIS JOURNAL, **36**, 48, 50; **37** 327.
[2] *Ibid.*, **36**, 32, 43.

best conditions, and it is characteristic of them that, after some hours, they begin to decline. Sometimes the decline, once begun, is continuous. At other times it is intermittent, each period of decline being followed by one of rising pressure.

Table XXX.—Cane Sugar.

Series III.

Weight-normal concentration.	Number of experiment.	Upward movement of manometer. mm.	Loss in rotation. Degrees.	Loss in rotation. Percentage.	Correction for inversion. Atmosphere.
0.1	1	0.07	0.20	1.60	0.03
"	2	0.07	0.10	0.80	0.01
"	3	0.09	0.05	0.39	0.01
"	4	0.09	0.10	0.79	0.01
0.2	1	0.05	0.15	0.61	0.02
"	2	0.05	0.15	0.60	0.02
0.3	1	0.06	0.50	1.37	0.07
"	2	0.06	0.60	1.64	0.08
0.4	1	0.08	0.55	1.15	0.08
"	2	0.07	0.60	1.25	0.08
"	3	0.22	0.40	0.83	0.06
"	4	0.04	0.40	0.83	0.06
0.5	1	0.24	0.90	1.53	0.13
"	2	0.22	1.00	1.70	0.14
"	3	0.07	1.05	1.71	0.15
"	4	0.38	0.75	1.29	0.11
0.6	1	0.48	1.20	1.73	0.12
"	2	0.10	1.30	1.86	0.14
0.7	1	0.61	1.20	1.51	0.18
"	2	0.45	1.10	1.39	0.16
0.8	1	0.01	1.55	1.74	0.23
"	2	0.34	1.60	1.80	0.24
0.9	1	0.44	1.85	1.88	0.29
"	2	0.05	1.95	1.98	0.30
1.0	1	0.23	2.90	2.71	0.46
"	2	0.59	3.50	3.26	0.56
"	3	0.91	2.00	1.87	0.31
(1)	(2)	(3)	(4)	(5)	(6)

Such conduct on the part of leaky cells is not difficult to explain. There is, apparently, in these cases a period, more or less prolonged, during which the intake of water through the

membrane is in equilibrium with the escape of solution from the cell, and the pressure therefore remains constant. As soon, however, as the solution becomes diluted to such an extent that it can, on further dilution, no longer maintain the

Table XXXI.—Cane Sugar.

Series III.

Weight-normal concentration.	No. of experiment.	Calculated gas pressure.	Osmotic pressure. 1. If all loss in rotation is ascribed to invers'n.	2. If all loss in rotation is ascribed to dilution.	3. If half the loss in rotation is ascribed to dilution.
0.1	1	2.23	2.42	2.51	2.48
"	2	2.23	2.44	2.48	2.46
"	3	2.23	2.37	2.39	2.39
"	4	2.23	2.38	2.42	2.41
0.2	1	4.46	4.76	4.83	4.80
"	2	4.46	4.75	4.81	4.79
0.3	1	6.69	7.02	7.20	7.14
"	2	6.68	7.03	7.25	7.18
0.4	1	8.91	9.29	9.49	9.43
"	2	8.92	9.26	9.47	9.40
"	3	8.92	9.30	9.45	9.41
"	4	8.91	9.25	9.40	9.35
0.5	1	11.14	11.53	11.84	11.75
"	2	11.14	11.59	11.96	11.85
"	3	11.14	11.65	12.03	11.91
"	4	11.14	11.68	11.96	11.87
0.6	1	13.37	14.00	14.39	14.25
"	2	13.37	13.97	14.40	14.25
0.7	1	15.60	16.47	16.92	16.78
"	2	15.60	16.55	16.97	16.83
0.8	1	17.82	18.93	19.52	19.34
"	2	17.83	18.89	19.51	19.32
0.9	1	20.06	21.64	22.37	22.15
"	2	20.05	21.56	22.33	22.10
1.0	1	22.28	24.07	25.23	24.87
"	2	22.28	23.98	25.41	24.98
"	3	22.29	23.96	24.74	24.50
(1)	(2)	(3)	(4)	(5)	(6)

pressure, a fall of the mercury in the manometer sets in, which may be, and often is, interrupted by a subsequent rise due to the repair of the membrane by the membrane-forming salts

which are always present. The mercury, however, in such cases never quite reaches the point from which the previous decline set in. It may, nevertheless, after having reached its highest point, remain stationary for a considerable time, showing that the intake of water and the escape of solution are again temporarily in equilibrium.

Formerly we did not rely upon the ability of the membranes to develop continuously the maximum pressures, and to sustain them for long periods, as the only test of the soundness of the membranes. We also carefully examined the liquid in

Table XXXII.—Cane Sugar. Mean Value for Each Concentration.

Series III.

Weight-normal concentration.	Temperature.	Calculated gas pressure.	Osmotic pressure. 1. If all loss in rotation is ascribed to invers'n.	2. If all loss in rotation is ascribed to dilution.	3. If half the loss in rotation is ascribed to dilut'n.
0.1	0°.24	2.23	2.40	2.45	2.44
0.2	0°.26	4.46	4.76	4.82	4.80
0.3	0°.22	6.69	7.03	7.23	7.16
0.4	0°.24	8.92	9.28	9.45	9.40
0.5	0°.21	11.14	11.61	11.95	11.85
0.6	0°.22	13.37	13.99	14.40	14.25
0.7	0°.21	15.60	16.51	16.95	16.81
0.8	0°.22	17.83	18.99	19.52	19.33
0.9	0°.27	20.06	21.60	22.35	22.13
1.0	0°.25	22.28	24.00	25.13	24.78
(1)	(2)	(3)	(4)	(5)	(6)

which the cell is immersed during an experiment for evidences of the presence of the substance whose pressure had been measured. The result was to convince us that the conduct of the cell in the bath may be relied upon to reveal any defects of the membrane or of cell construction.

If our membranes did not leak, the dilution of the cell contents was due, in the main, to the causes so frequently mentioned in former papers,[1] namely: 1. The slipping of the manometer in the stopper, or the crowding upwards of both manometer and stopper when the former could not slip in the lat-

[1] THIS JOURNAL, **36**, 24, 26, 48; **37**, 327.

ter; 2. The sucking in of water from the wall while the cell was being closed for a measurement, and again while it was being taken apart after an experiment.

The first of these difficulties, *i. e.*, dilution due to displace-

Table XXXIII.—Cane Sugar.

Series III.

Weight-normal concentration.	No. of experiment.	Calculated gas pressure.	Ratio of osmotic to gas pressure. 1. If all loss in rotation is ascribed to inversion.	2. If all loss in rotation is ascribed to dilution.	3. If half the loss in rotation is ascribed to dilut'n.
0.1	1	2.23	1.085	1.126	1.112
"	2	2.23	1.094	1.112	1.103
"	3	2.23	1.063	1.072	1.072
"	4	2.23	1.067	1.085	1.081
0.2	1	4.46	1.067	1.083	1.076
"	2	4.46	1.065	1.078	1.074
0.3	1	6.69	1.049	1.076	1.067
"	2	6.68	1.052	1.085	1.075
0.4	1	8.91	1.043	1.065	1.058
"	2	8.92	1.038	1.062	1.054
"	3	8.92	1.043	1.059	1.055
"	4	8.91	1.038	1.055	1.049
0.5	1	11.14	1.035	1.063	1.055
"	2	11.14	1.040	1.074	1.064
"	3	11.14	1.046	1.080	1.069
"	4	11.14	1.048	1.074	1.066
0.6	1	13.37	1.047	1.076	1.066
"	2	13.37	1.045	1.077	1.066
0.7	1	15.60	1.056	1.085	1.076
"	2	15.60	1.061	1.088	1.079
0.8	1	17.82	1.062	1.095	1.085
"	2	17.83	1.059	1.094	1.084
0.9	1	20.06	1.079	1.115	1.104
"	2	20.05	1.075	1.114	1.102
1.0	1	22.28	1.080	1.132	1.116
"	2	22.28	1.076	1.140	1.121
"	3	22.29	1.075	1.110	1.099
(1)	(2)	(3)	(4)	(5)	(6)

ments of manometers and stoppers, has been overcome through improvements in method and manipulation. To what extent the remedy has been effective is shown in Table XXX.,

column 3, in which are recorded the total upward movements of the manometers in the present series of experiments. It will there be seen that the displacement was in no case sufficient sensibly to affect the concentration of the cell contents.

Unfortunately, however, the measures which were taken to secure the manometers and stoppers more firmly in their places have prolonged somewhat the time within which a cell can be closed and opened, so that dilution due to the second cause mentioned above is probably a little greater now than formerly.

Table XXXIV.—Cane Sugar. Mean Values for Each Concentration.

Series III.

Weight-normal concentration.	Temperature.	Calculated gas pressure.	Ratio of osmotic to gas pressure. 1. If all loss in rotation is ascribed to invers'n.	2. If all loss in rotation is ascribed to dilution.	3. If half the loss in rotation is ascribed to dilution.
0.1	0°.24	2.23	1.077	1.099	1.092
0.2	0°.26	4.46	1.067	1.081	1.075
0.3	0°.22	6.69	1.051	1.081	1.071
0.4	0°.24	8.92	1.040	1.060	1.054
0.5	0°.21	11.14	1.042	1.073	1.064
0.6	0°.22	13.37	1.046	1.077	1.066
0.7	0°.21	15.60	1.058	1.087	1.078
0.8	0°.22	17.83	1.060	1.095	1.085
0.9	0°.27	20.06	1.077	1.115	1.103
1.0	0°.25	22.28	1.077	1.127	1.112
(1)	(2)	(3)	(4)	(5)	(6)

The losses of rotation which the solutions suffered while in the cells are all brought together in Table XXX., where they are stated in the form of saccharimeter degrees (column 4) and in that of percentages of original rotation (column 5). These values, in our judgment, are the extreme measure of the uncertainty of our determinations of osmotic pressure. The loss in rotation is due partly to inversion and partly to dilution, and it is impossible to ascertain with any satisfactory degree of certainty how much of it is to be ascribed to either

of the two causes. The correction for inversion,[1] when applied to the observed pressure, lowers it, while that for dilution raises it; that is, the two corrections are of a compensating character.

In column 6 of Table XXX. are given, in fractions of an atmosphere, the corrections for each experiment if all the observed loss in rotation is ascribed to inversion and no allowance is made for dilution. These are the quantities which have been subtracted from the observed pressures as corrections in all the tables from I. to XXX. The results are unquestionably somewhat too low because a part of the loss of rotation, all of which has hitherto been ascribed to inversion, was due to dilution, the correction for which, if it could be applied, would be added to the observed pressures.

In order to show the effect of corrections for dilution, Tables XXXI. and XXXII. have been added. The former gives the results of the individual experiments as they would stand:

1. If all loss of rotation is ascribed to inversion and no correction is made for dilution (column 4).

2. If all loss in rotation is ascribed to dilution and no correction is made for inversion (column 5).

3. If one-half the observed loss in rotation is ascribed to dilution and no account is taken of inversion.

In Table XXXII. the same data are presented in condensed form as mean values for each concentration.

Just as the results given in column 4 (Tables XXXI. and XXXII.) are too low because no account is taken of *dilution*, so are those in column 5 too high, because no correction for *inversion* has been made. In the earlier work[2] it was attempted to determine by the method of Fehling the amount of the inversion which takes place in the cell, and the attempt has since been repeated, but without convincing results. It may be stated, however, that, though evidences of inversion are never wanting when the test is applied to a solution, after its removal from the cell, the largest amount which appeared to be found by the method of Fehling has not exceeded, even in

[1] THIS JOURNAL, **36**, 41.
[2] *Ibid.*, **34**, 30.

weight-normal solutions, the quantity which, as a correction for observed pressures, would be equivalent to 0.05 atmosphere. In other words, if the indications obtained by the Fehling method are even approximately quantitative, the values recorded in column 6 of Table XXX., as corrections, are considerably too large, and the pressures given in column 4 in Tables XXXI. and XXXII. are accordingly, to an equal degree, too low.

The reason for introducing column 6 (Tables XXXI. and XXXII.) requires explanation. In this are presented the pressures for the various weight-normal concentrations of solution as they would stand if the observed pressures were corrected for one-half the loss of rotation, without any correction for inversion. In our judgment, the values in column 6 are still somewhat too high. The basis for this opinion will be found in the following explanation: The time now required to close a cell—*i. e.*, the time elapsing between the filling in of the solution and the screwing down of the manometer nut—varies from 8 to 15 minutes, and the time usually spent in opening the cell at the close of an experiment—*i. e.*, the time from the loosening of the manometer nut to that of emptying the cell—is about the same, that is, it varies from 8 to 15 minutes. Whatever dilution of the cell contents occurs during the closing of the cell affects the observed pressure, while that which occurs during the opening of it does not. Hence, before correcting the observed pressures for loss in rotation, that portion of it which is due to dilution occurring during the opening of the cell should be deducted. We have no means, however, of ascertaining what proportion of the whole dilution, as measured by loss of rotation, is to be thus deducted. But it is safe to assume that more than half of the dilution occurs subsequent to the measurement of pressure; for, during the period in which the cell is being closed, the contents are all the time under increased pressure, while during the time in which it is being opened, they are as constantly under strongly diminished pressure. We have, therefore, ventured to deduct one-half of the observed loss of rotation before correcting the observed pressures for dilution

and to present the results in column 6 of Tables XXXI. and XXXII. We also venture to predict that, when we remeasure the osmotic pressure of cane sugar solutions in the vicinity of 0°, after having so improved our cells as nearly to suppress dilution, we shall find pressures for the various concentrations which lie between those recorded in columns 4 and 6 of Tables XXXI. and XXXII. In other words, we judge that the measurements as presented in column 4 of the tables are still uncertain only within the limits indicated below:

Weight-normal concentration.	Limit of uncertainty.	
	Atmosphere.	Percentage.
0.1	0.04	1.66
0.2	0.04	0.84
0.3	0.13	1.85
0.4	0.12	1.29
0.5	0.24	2.07
0.6	0.26	1.86
0.7	0.30	1.82
0.8	0.34	1.79
0.9	0.53	2.45
1.0	0.78	3.25

It is obvious that if the assumption that more dilution occurs while the cells are being opened than while they are being closed is correct, later work under better conditions can only tend to diminish the magnitude of the now uncertain values recorded above, for any correction whatever for inversion will diminish the values given in column 6 of Tables XXXI. and XXXII., while any correction of previously underestimated dilution occurring during the process of opening the cell will raise the values in column 4.

We have endeavored in two ways to secure some safe basis for judgment in respect to the matters discussed above. In the first place, in order to ascertain whether a considerable proportion of the loss in rotation is due, as was suspected, to dilution rather than to inversion, the cells, just before they were closed, and again just before they were opened, were dipped, in many instances, in a solution of sugar whose concentration was the same as that of the solution under investiga-

tion. In all such cases, the loss of rotation was much less than —often less than half—that of solutions in cells which had not been so treated, provided no unusually long time was consumed in the closing and opening processes. It is hardly necessary to state that cells which had been dipped were carefully cleansed externally before placing them in the bath. The practice of dipping has proved so efficacious as a means of reducing loss of rotation that it is now employed with all cells.

Again, in order to discover, if possible, whether more dilution occurs while opening than while closing the cells, a record of the time consumed in each performance has been kept, and this shows that the loss in rotation is affected more by any unusual prolongation or shortening of the time employed in the former than in the latter operation.

The most important fact which has been brought out by this series of measurements is that the osmotic pressure of cane sugar solutions, in the vicinity of the freezing point of the solvent, considerably exceeds the calculated gas pressures for the same temperatures. Tables XXXIII. and XXXIV. have been introduced in order to facilitate a comparison of the two sets of values. In them the ratios of osmotic to gas pressures are given in three ways (columns 4, 5, and 6), according to each of the possible methods of correcting the observed pressures for the loss in rotation which occurs in the cell. The fact of an excess of osmotic over gas pressure at low temperatures appears to be established whatever may be the view which is accepted as to the proper method of correcting the observed pressures for loss in rotation.

Any attempt to explain the apparently abnormal(?) pressures of cane sugar solutions in the vicinity of 0° would be premature at the present time, and any discussion of the question must continue to be unprofitable until a much larger number of pertinent facts have been firmly established by experiment. Some may see in the high pressures which have been obtained an evidence of the hydration of cane sugar in solution, and may point to the abnormal(?) freezing points of such solutions as a confirmation of the correctness of this view. But, as we shall show in our next communication, the osmotic pres-

sures of glucose solutions in the vicinity of 0° also exceed the calculated gas pressures for the same temperatures, and this despite the fact that whatever evidence can be secured from the freezing points is to the effect that glucose in solution is not hydrated.[1]

Others may discover in the high pressures in question, and in the fact that they are, in a general way, nearly equal to those which were obtained in the vicinity of 20°, a suggestion that osmotic pressure, unlike that of gases, *has little or no temperature coefficient.* But an equally just suspicion, apparently, is that somewhere between 0° and 20° a temperature may be found at which osmotic pressure, like the volume of the solvent, is at a *minimum*, and from which it increases, with change of temperature, in both directions. Our methods are probably already sufficiently accurate to enable us to determine with certainty whether such a minimum exists, and we have, accordingly, begun a series of measurements at temperatures between 0° and 20°.

Attention is called to a peculiarity of the ratios in columns 4, 5, and 6 of Table XXXIV. It will there be seen that the ratio of osmotic to gas pressure in case of cane sugar appears to reach a minimum with the 0.4 weight-normal solution. It was the appearance of this relation which induced us to make a larger than usual number of measurements of the pressures of the 0.1, 0.4, and 0.5 normal solutions (see Table XXXIII.). We do not, however, regard the reality of this apparent minimum ratio as established. It was stated in a former paper[2] that some uncertainty exists as to the exact osmotic equivalence of the small quantities of membrane-forming salts which are employed in connection with the measurements of pressure; that, if the evidence of the freezing points is reliable, the ferrocyanide is dissociated into 8 instead of 5 ions. If this is true, the osmotic pressure of the ferrocyanide within the cell is probably slightly greater than that of the copper sulphate in the water in which the cell is immersed, and a slight correction should be made for the inequality. The correction, if one is to be made, is small, owing to the smallness of the quan-

[1] THIS JOURNAL, 37, 360.
[2] *Ibid.*, 36, 33.

tities of the membrane-forming salts which are used, but it may be of sufficient magnitude to affect sensibly the ratio in question in the case of the most dilute solutions. Its effect upon the ratios would, of course, be inversely proportional to the concentration of the solutions. We have delayed attacking, except in a superficial way, the problem of a possible slight osmotic inequality of our membrane-forming salts until we could complete the preparations, now in progress, for the simultaneous determination of the osmotic pressure and of the dissociation of electrolytes.

JOHNS HOPKINS UNIVERSITY,
February 1, 1907.

ON SOME CUPRAMMONIUM SALTS. III.[1]

BY DAVID W. HORN.

The object of this paper is to present further evidence of the correctness of the point of view presented in the previous communication.[2]

Cuprammonium salts are known that correspond to each of the following formulae:

$Cu(Ac')_2.NH_3$;
$Cu(Ac')_2.2NH_3$;
$Cu(Ac')_2.4NH_3$;
$Cu(Ac')_2.5NH_3$;
$Cu(Ac')_2.6NH_3$.

That the number of salts represented by some of these formulae is small may be attributed to the limited knowledge of this group of compounds.

When this study of cuprammonium salts began, there was no general theory that accounted satisfactorily for all these various types. The idea expressed in text-books and elsewhere that cuprammonium salts conform to 2 types,

$$Cu(NH_3)_2(Ac')_2 \quad \text{and} \quad Cu(NH_3)_4(Ac')_2,$$

has not only proved unproductive, but also misleading. There

[1] Read in abstract before the Philadelphia Section, American Chemical Society, Oct. 18, 1906.

[2] THIS JOURNAL, **35**, 271 (1906).

have never been data available to suggest the way in which Werner's conceptions, in their original form, could be used to account for salts of the general formulae,

$$Cu(Ac')_2.NH_3 \quad \text{and} \quad Cu(Ac')_2.5NH_3.$$[1]

The recent attempt made by Pfeiffer[2] to modify Werner's conceptions so as to include all cuprammonium salts rests upon so many assumptions that its value may be seriously questioned. However, without some general conception of these compounds it is difficult to see how any considerable advance in knowledge of them could be made.

As stated in the preceding paper, in the work that has been in progress in this laboratory for some time, cuprammonium salts are studied with reference to the equilibria in the systems in which the salts form. It was there shown that this point of view has distinct advantages over previous ones in that cuprammonium salts formed from anhydrous copper salts and dry ammonia gas are included logically in the same class as those formed in solutions, and in that all necessity for regarding cuprammonium salts of any degree of complexity as abnormal or unusual is thus removed.

From this point of view, at any one temperature, the complexity of a cuprammonium compound is dependent partly upon the concentrations of ammonia, copper salt and water in the system where it forms, and partly upon the nature of the acid residue. It has been shown previously how the data then available suggested this view as a probable one.

The experiments in the present paper show more definitely than was possible before, the dependence of the complexity of a cuprammonium compound upon the concentration of ammonia, copper salt and water in the system where it forms. More definite treatment of the specific effect of the acid residue will be given in a later paper.

Prior to the appearance of my previous paper, Kohlschütter[3] had given additional weight to the idea that there are *two* types to which cuprammonium compounds conform, an idea

[1] Z. anorg. Chem., 3, 303 (1893).
[2] *Ibid.*, 48, 98 (1905).
[3] Ber. d. chem. Ges., 37, 1153 (1904).

that has always had a retarding influence on the development of knowledge of these compounds. Consequently, I then called attention to Kohlschütter's work and presented the cuprammonium oxalates as prima facie evidence against the two-type idea and as directly suggestive of the point of view that I then discussed. Kohlschütter has since[1] adopted the suggestion, in a limited way, in his recent study of thiocarbamid compounds of cuprous salts, and has proposed the name "Atomaffitat" to account for the effect of the acid residue. This indefinite term seems to add little, if anything, but obscurity to a subject already obscure because of the small amount of data available.

From the point of view of the equilibrium involved, there should be for each temperature a series of definite ratios,

$$x \text{ mols. } NH_3 : y \text{ mols. } Cu(Ac')_2 : z \text{ mols. } H_2O,$$

which would permit the formation of a cuprammonium salt of one degree of complexity and exclude the possibility of formation of a salt of any other degree of complexity. As the values of x, y and z change, the ratio should approach limits beyond which the favored salt could no longer form, but in its place a more or less complex salt would appear.

The simplest case for the experimental test of this reasoning would consist of 2 cuprammonium salts, both of which could be obtained from aqueous solutions without "water of crystallization." As fulfilling these conditions, the salts

$$Cu(SCN)_2.2NH_3 \quad \text{and} \quad Cu(SCN)_2.4NH_3$$

were selected.

Some discussion of the preparation and properties of these salts appears later in this paper, along with analyses that serve for identification.

To determine the unknown values in the ratio

$$x \text{ mols. } NH_3 : y \text{ mols. } Cu(Ac')_2 : z \text{ mols. } H_2O,$$

corresponding to the stability of each salt, the solid salts, freshly prepared, were shaken, at constant temperature, with ammonia water of different concentrations until the concentrations

[1] Ann. Chem. (Liebig), **349**, 252 *et seq.* (1906).

of ammonia and copper salt in the resulting solutions became constant. Weighed quantities of the saturated solutions were then analyzed for ammonia and thiocyanion and water was calculated by difference.

The results obtained in this way, at 25°, appear in the table on the opposite page.

When the figures (in the last two columns) corresponding to the values of x' and y' in the ratio

$$x' \text{ mol. } NH_3 : y' \text{ mol. } Cu(SCN)_2 : 1000 \text{ mol. } H_2O,$$

are plotted to show the interdependence of the concentrations of ammonia and copper salt at constant concentration of water, the solubility curve shown in the following figure, I., is obtained:

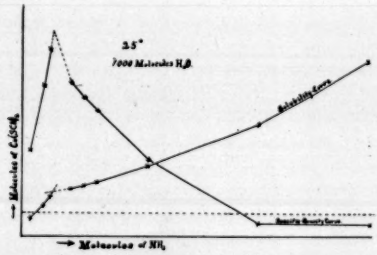

Fig. I.

The 2 parts of this solubility curve show clearly that the interdependence referred to is quite different for the 2 different salts in contact with their saturated solutions. The 2 parts of the curve prove the existence of 2 distinct series of definite ratios,

$$x \text{ mols. } NH_3 : y \text{ mol. } Cu(SCN)_2 : z \text{ mols. } H_2O,$$

any ratio of each series representing conditions under which 1, and only 1, of the 2 cuprammonium salts can exist, in stable equilibrium, at the given temperature. Any ratio of each

Table I.—Solubility of Copper Sulphocyanate in Ammonia Water at 25°.

No. of solution.	One gram of solution contains			One hundred molecules of the mixture contain			One thousand molecules of water dissolve		Composition of solid salt in contact with solution.
	gram NH_3.	gram $Cu(SCN)_2$.	gram H_2O.	x mols. NH_3.	y mols. $Cu(SCN)_2$.	z mols. H_2O.	x' mols. NH_3.	y' mols. $Cu(SCN)_2$.	
1	0.2147	0.1522	0.6331	25.90	1.74	72.34	358.04	24.09	
2	0.1655	0.1124	0.7221	19.24	1.24	79.50	242.02	15.60	
3	0.0993	0.0798	0.8209	11.23	0.86	87.92	127.76	9.74	$Cu(SCN)_2.4NH_3$
4	0.0639	0.0659	0.8702	7.14	0.70	92.15	77.51	7.59	
5	0.0535	0.0622	0.8843	5.98	0.66	93.36	64.05	7.04	
6	0.0426	0.0596	0.8978	4.75	0.63	94.63	50.21	6.65	
7	0.0250	0.0511	0.9239	2.76	0.54	96.72	28.55	5.55	
8	0.0198	0.0408	0.9394	2.17	0.42	97.41	22.27	4.35	$Cu(SCN)_2.2NH_3$
9	0.0079	0.0245	0.9676	0.85	0.25	98.89	18.61	2.54	

series then favors but one degree of complexity in cuprammonium sulphocyanates and excludes the possibility of stable existence of the cuprammonium sulphocyanate of the other degree of complexity. There is one ratio of which this is not true; it is the ratio common to both series and is the only ratio representing conditions under which both cuprammonium salts can exist side by side. This may be called the "transition ratio" for the 2 salts. It is represented by the "break" in the solubility curve.

As a check upon the probable existence of this unique condition in the saturated solution, corresponding to the transition ratio, the specific gravities of the saturated solutions were determined. The values obtained appear in the following table, II., in which the numbers in column 1 refer to the same solutions as the numbers in column 1, Table I.:

Table II.—Specific Gravities of Saturated Solutions at 25°.

Number of solution.	Molecules NH_3 present for every 1000 mols. H_2O.	Sp. gr. at 25° referred to water at 25°.	Sp. gr. minus 1.	$1000 \times$ (sp. gr. —1).
1	358.04	0.99853	0.00147	—1.5
2	242.02	0.99871	0.00129	—1.3
3	127.76	1.00703	0.00703	7.0
4	77.51	1.01336	0.01336	13.4
5	64.05	1.01506	0.01506	15.1
6	50.21	1.01705	0.01705	17.1
7	28.55	1.02132	0.02132	21.3
8	22.27	1.01661	0.01661	16.6
9	8.61	1.00816	0.00816	8.2

In Fig. I., the curve marked "specific gravity curve" represents the interdependence of the specific gravity and the concentration of ammonia in the ratios mentioned above. For purposes of graphic representation the values actually plotted are not the specific gravities but the specific gravities *minus* 1. The dotted axis in the figure is the axis of abscissae for the specific gravity curve; the axis of ordinates coincides with the corresponding axis for the solubility curve.

It is evident that the saturated solution represented by "the transition ratio" is unique in occupying a *minimum* volume,

and that the existence of the 2 distinct series of ratios shown by the solubility curve is confirmed by the specific gravity curve.

It was pointed out in the previous paper that one necessary condition in considering cuprammonium salts from the point of view suggested is that the temperature shall be the same in all cases. There was sufficient reason for believing that the extent and character of the series of ratios corresponding to any one salt would vary with the temperature. In the following table, III., are given the results of the analyses of saturated solutions prepared at 40°.

In Fig. II. these results are plotted just as the results at 25° were plotted in Fig. I. A comparison of the 2 solubility

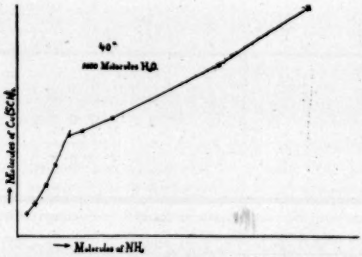

Fig. II.

curves shows definitely the variations of the 2 series of ratios and of the transition ratio with the temperature.

This study of the sulphocyanates was made to test the correctness of the point of view we had adopted, and can be regarded only as of a preliminary character. It is safe to predict, however, that the results will all be of the same general character when suitable salts are at hand and the work is extended to include cuprammonium salts of the various hydrated and anhydrous types.

Table III.—Solubility of Copper Sulphocyanate in Ammonia Water at 40°.

Number of solution.	One gram of solution contains			One hundred molecules of the mixture contain			One thousand molecules of water dissolve		Composition of solid salt in contact with solution.
	gram NH_3.	gram $Cu(SCN)_2$.	gram H_2O.	x mols. NH_3.	y mols. $Cu(SCN)_2$.	z mols. H_2O.	x' mols. NH_3.	y' mols. $Cu(SCN)_2$.	
10	0.1802	0.1976	0.6222	22.89	2.38	74.73	306.28	31.83	
11	0.1398	0.1658	0.6944	17.23	1.93	80.84	213.10	23.93	
12	0.0758	0.1299	0.7943	9.04	1.47	89.49	101.00	16.38	$Cu(SCN)_2.4NH_3$
13	0.0550	0.1207	0.8243	6.50	1.35	92.15	70.59	14.67	
14	0.0435	0.1178	0.8388	5.13	1.32	93.56	54.82	14.07	
15	0.0352	0.0876	0.8772	4.04	0.95	95.01	42.53	10.00	
16	0.0257	0.0655	0.9088	2.89	0.70	96.41	30.00	7.22	$Cu(SCN_2).2NH_3$
17	0.0177	0.0418	0.9405	1.94	0.44	97.63	19.86	4.46	
18	0.0094	0.0281	0.9625	1.02	0.29	98.69	10.31	2.93	

This prediction is made upon the basis of the Phase Rule. In all cases like this one the systems studied will be of the third order, with ammonia, copper salt and water as the components. In systems where a cuprammonium salt of but one degree of complexity can form there will be 3 phases: 1 solid, the cuprammonium salt; 1 liquid, the saturated solution; and 1 vapor phase, a mixture of ammonia and water vapor. All such systems will be divariant like the 2 series of systems we have studied.

In such divariant systems the state of the system is perfectly defined when 2 of the 3 factors, pressure, temperature, or concentration, of the components in the liquid phase are arbitrarily fixed. The concentration of the components in the vapor phase is dependent directly upon their concentration in the liquid, and the concentration of the components in the solid phase is fixed by the law of definite proportions. In our study of the sulphocyanates we have fixed arbitrarily the temperature and the concentration of ammonia and water, 2 out of the 3 interdependent concentrations, in the liquid phase. In such divariant systems, according to the Phase Rule, there must be, for every arbitrarily selected temperature, a series of concentration ratios of the components in the liquid phase, corresponding to stable equilibrium in the system, and for every arbitrarily selected concentration ratio, a series of temperatures. The existence of the series of ratios for each temperature has already been shown for each of the sulphocyanates, and the existence of a series of temperatures for each ratio will be shown in Fig. III.

When a new salt appears in such a system, the system becomes monovariant, and for each arbitrarily selected temperature there can be but *one* concentration ratio of the components in the liquid phase that will satisfy conditions for stable equilibrium, *i. e.*, "the transition ratio."

As a special case under the Phase Rule, the comparatively limited data presented in this paper may be generalized graphically[1] to show more clearly the interdependence of temperature, concentration ratio and complexity of cuprammonium salt.

[1] Compare Roozeboom and Schreinemakers: Z. physik. Chem., 15, 595 (1894). "Gleichgewichte in System: Wasser, Chlorwasserstoff, Eisenchlorid."

In Fig. III., the XT-plane is the plane of zero concentration of copper salt; the YT-plane, the plane of zero concentration of ammonia; and the T-line in which the 2 planes intersect at right angles to each other is the temperature axis along which rising temperature is measured in the direction of the

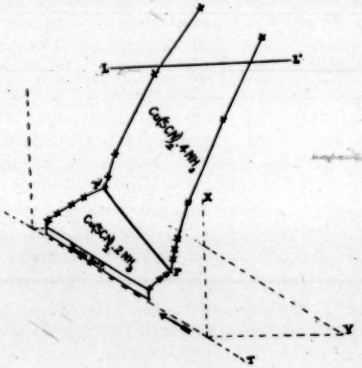

Fig. III.

arrow, the XY-plane being parallel to the plane of zero temperature. The figure is drawn to scale. Within the limits of concentration and temperature observed in the experiments, the 2 surfaces represent all conditions of concentration and temperature under which the 2 sulphocyanates can exist in contact with their solutions in aqueous ammonia. The line PP′ is the path of the transition ratio as temperature changes.

By the aid of the figure it is possible to indicate, with a fair degree of probability, certain things that would be found to be true beyond the limits of the experiments. The true outer limit of the surface for the salt $Cu(SCN)_2.4NH_3$ must remain unknown, for it is possible, experimentally, to get only a limited amount of ammonia into any aqueous solution at a fixed tem-

perature. The more elevated the temperature for any known aqueous solution, the less ammonia can be dissolved. The limit actually imposed on the surface for the salt,

$$Cu(SCN)_2.4NH_3,$$

then, must, at constant concentration of copper salt, incline, with rising temperature, toward the YT-plane, let us say parallel to LL′, so that the surface must grow narrower as the temperature rises. It is evident from the figure that the surface for the salt $Cu(SCN)_2.2NH_3$ grows broader with rising temperature. If both salts continue in existence as the temperature rises, a temperature is indicated by the figure where the surface for the more complex salt will have diminished to a point, and beyond which only the less complex salt can exist. Conversely, a low temperature is indicated by the figure, beyond which it would be impossible to prepare the less complex salt from aqueous solution.

The one limit of the surface for the salt $Cu(SCN)_2.2NH_3$ is the line PP′, the path of the transition ratio. The other limit corresponds to the appearance of a basic salt. The salt $Cu(SCN)_2.2NH_3$ is *insoluble* in water, but soluble in water that contains a small amount of ammonia. If a solution of the salt in dilute ammonia water is diluted with water a basic salt of pale blue-green color is precipitated when a certain definite dilution is reached. This precipitate always forms at the same dilution, at constant temperature, as we have found in analogous experiments with cuprammonium sulphate. There must be, then, for each temperature, a transition ratio for the basic salt and the salt $Cu(SCN)_2.2NH_3$, and with rising temperature there must be a change in this transition ratio, the path of which, represented graphically, will be the other limit to the surface for the salt $Cu(SCN)_2.2NH_3$. For a fixed concentration of ammonia and of water the decomposition into basic salt (hydrolysis) will be greater the higher the temperature, so that it is probable that the limit of the surfaces for $Cu(SCN)_2.2NH_3$ and the basic salt inclines toward the XT-plane and accentuates the broadening of this plane with rising temperature and its narrowing with falling temperature.

This limit lies near the values realized in the experiments in the most dilute solutions.

Considering some of the changes possible in any concentration ratio,

$$x \text{ mol. } NH_3 : y \text{ mol. } Cu(SCN)_2 : z \text{ mol. } H_2O,$$

it is clear that x, y, or z might diminish until it approached to or equaled zero. When $z = 0$ we have for study the formation of cuprammonium sulphocyanates from anhydrous copper sulphocyanate and dry ammonia. So that, in general, the formation of cuprammonium salts from anhydrous copper salt and dry ammonia is only a special case, the limiting case, of the formation of all of the ammonia compounds, hydrated and anhydrous, of the given copper salt.[1]

This direct relation could have been shown graphically if we had plotted the values in columns 5, 6 and 7, Tables I. and III., in the triangular diagram[2] that is frequently used for isotherms in ternary systems, but the numerical values of y, the mols. of copper sulphocyanate, are so small that the graphs are less satisfactory than Figs. I. and II., and their combination, than Fig. III. The relation in the general case is readily seen from Fig. IV., where the pure components are represented

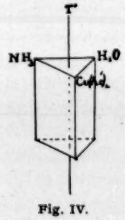

Fig. IV.

at the angles of a triangular right prism,[3] within which all concentration ratios of the 3 components may be plotted at temperatures measured along the perpendicular axis of the

[1] Cf. THIS JOURNAL, 35, 284 (1906).
[2] Gibbs: T. Conn. Acad., 3, 176 (1876).
[3] *Vide* Ostwald: Lehrb. d. Alge. Chem., II, 2, 982 *et seq.*

prism. One of the lateral faces, it will be seen, is a part of the diagram that would represent the formation of cuprammonium salts from anhydrous copper salt and dry ammonia; another, a part of the diagram that would represent the formation of hydrated copper salts from anhydrous copper salt and water. Of course, the partial character of these planes, as compared with the diagrams of which they are a part, is due to the fact that they represent systems only at one pressure, the average pressure of solubility determinations, about 1 atmosphere. The influence of pressure cannot be neglected in the formation of hydrates and of cuprammonium salts in the absence of water, as it may be in solubility work, where its effect is so small. I have already made some progress in the study of systems consisting of anhydrous copper salt and dry ammonia, but am not ready to discuss the experiments.

Further consideration of the effect of the acid residue will show that the ideas advanced represent a special case in the general problem of complex compounds. The nature of the metal, the acid residue, or the addendum, may vary, while the 2 remaining factors in the complex molecule are unchanged. In cuprammonium salts the metal and the addendum remain the same while the acid residue varies; consequently, when the temperature is fixed, the specific effect of the acid residue is the other influence, besides concentration, that affects the complexity. In a comparison of the properties of the complex compounds of any one copper salt with different addenda, as ammonia, pyridine, ethylenediamine, water, etc., the specific effect of the addendum takes the place of that of the acid residue. When a comparison between cuprammonium chloride, cadmium ammonium chloride, zinc ammonium chloride, nickel ammonium chloride, etc., is made, the specific effect of the metallic atom takes the place of that of the acid residue.

The case of cuprammonium salts is less simple than some others because the compounds frequently form in aqueous solution, where the solvent decomposes the compound to an extent proportional to the relative concentration of the solvent, and where the solvent may act as an addendum.

Preparation and Properties of the Sulphocyanates.

1. CUPRIDIAMMONIA SULPHOCYANATES.

This salt may be prepared by dissolving cupric sulphocyanate in dilute ammonia water, or by digesting cuprous sulphocyanate and dilute ammonia water in contact with the air;[1] also by treating solutions of potassium or ammonium sulphocyanates with ammonia water and solutions of cupric salts, provided all the solutions are "dilute."[2] The salt is readily obtained from the solutions on standing in the air or over sulphuric acid in a desiccator. It is quite pure when first separated, and is sufficiently stable to be dried in the air. Long-continued exposure to the air results in its decomposition. The salt is not soluble in water, although it has been stated that this is the case.[3] The compound appears in gray-blue needles, the color of which, when dry, is suggestive of gun-metal. Under the polarizing microscope the crystals invariably exhibit parallel extinction and the biaxial brush, so that they are probably orthorhombic. The following analysis of a specimen that had been preserved in a bottle about 6 weeks served for identification.

Salt taken for analysis. Gram.	Standard acid neutralized. cc.	Percentage of ammonia found.	Percentage of ammonia calculated for $Cu(SCN)_2.2NH_3$.
0.4723	20.64	15.86	15.95
0.4598	20.09	15.86	

2. CUPRITETRAMMONIUM SULPHOCYANATE.

This salt was first prepared by T. W. Richards and Merigold.[4] As the method they used has been shown to be unnecessarily complicated, it need not be given. The same salt is obtained when a cupric salt is dissolved in "strong" ammonia water and treated with a solution of potassium or ammonium sulphocyanate.[5]

The following conditions furnish readily a good yield of

[1] Meitzendorff: Pogg. Ann., **36**, 92 (1842).

[2] Litterscheid: Arch. der Pharm., **239**, 336 (1901). Kohlschütter: Ber. d. chem. Ges., *loc. cit.*

[3] *Vide* Meitzendorff: *Loc. cit.*, and Litterscheid: *Loc. cit.*

[4] Z. anorg. Chem., **17**, 250 (1898).

[5] Litterscheid: *Loc. cit.*; Kohlschütter: *Loc. cit.*

the salt: To a solution of 250 grams of crystallized copper sulphate, $CuSO_4.5H_2O$, in 800 cc. of water, warmed to about 60°, add 300 cc. of ammonia water, sp. gr. 0.9. To 162 grams of ammonium thiocyanate, in 200 cc. of water warmed to about 60°, add 100 cc. of ammonia water, sp. gr. 0.9. Mix the 2 solutions and filter rapidly. The salt separates from the filtrate within a short time.

The salt is very unstable in the air, and its instability is increased by small amounts of impurity. It can be recrystallized from ammonia water, sp. gr. 0.9, by cooling, or by passing a current of air rapidly through the solution. The pure, dry salt has a measurable tension of ammonia over it, so that it cannot be kept pure for any length of time in a desiccator. The following analysis of a specimen recrystallized and kept for 2 days in a tight (?) desiccator over sticks of potassium hydroxide served for identification:

Salt taken for analysis. Gram.	Standard acid neutralized. cc.	Percentage of ammonia found.	Percentage of ammonia calculated for $Cu(SCN)_2.4NH_3$.
0.5456	44.67	27.25	27.52
0.3789	31.08	27.28	

The salt has the deep, purple-blue color of cupritetrammonium sulphate. It is soluble in water, but the dissolved salt is decomposed by great dilution with precipitation of a basic salt. The salt has been described as appearing in "rhombic plates." Its rapid decomposition makes its microscopic examination difficult, but it exhibits parallel extinction and a uniaxial interference figure. Some large crystals obtained from a solution that was losing ammonia very slowly confirmed the opinion that the crystals are hexagonal, and showed that they belong to the trapezohedral group.

EXPERIMENTAL METHODS.

The saturated solutions in the solubility determinations were made under conditions that have been described. Five hours' shaking usually sufficed for attaining equilibrium, though the solids were shaken with the solutions from 6.5 to 7.5 hours.

The saturated solutions were analyzed volumetrically.

In determining ammonia, quantities of the saturated solutions, from 2 to 5 cc., were weighed in 50 cc. measuring flasks and, after partial dilution, were treated with a little zinc dust. The copper is removed very rapidly, at ordinary temperatures, by the finely divided zinc. Each colorless solution thus obtained was diluted to the mark, shaken thoroughly and filtered through a small filter into a 25 cc. burette, due care being taken to discard the first filtrates. The titration was then made against a standard sulphuric acid, using methyl orange as indicator.

In determining thiocyanic acid, weighed quantities of the saturated solutions were analyzed by Volhard's method. This method had been used in ammoniacal copper solutions by Richards and Merigold.[1] There is no difficulty in its employment provided an excess of the standard silver nitrate is always added to the ammoniacal solutions before the excess of ammonia is neutralized with nitric acid. The silver nitrate solution was standardized by weighed quantities of cupridiammonium sulphocyanate, dissolved in ammonia water.

The distillation in the analysis of a cuprammonium salt for ammonia has been completely freed from "bumping" by adding some granulated tin, an effect more or less accomplished by the addition of lime[2] in our earlier analyses. The satisfactory action of the tin is independent of the presence of the copper that deposits on it when a cuprammonium salt is analyzed. Aluminium and zinc are not good substitutes for the tin because of the rapidity with which they react on the alkali. A comparison of the duplicate analyses of the sulphocyanates gives a fair idea of the accuracy attainable by the method when tin is used.

The specific gravity determinations were made by weighing a glass sinker, belonging to a Westphal balance, in freshly boiled water and in the saturated solutions, at 25°. The saturated solutions were placed in a narrow measuring cylinder that was always filled to the same mark, so that the fine wire suspending the sinker was always wet by the solutions to about

[1] *Loc. cit.*

[2] THIS JOURNAL, 32, 235 (1904).

the same extent. During a weighing the cylinder stood in the center of a large beaker of water at a temperature of 25°. The cylinder and beaker were kept in the thermostat when not in use, and the weighings were made as soon as possible after their removal from the thermostat. A large analytical balance was used. This method is capable of giving results that are accurate to the sixth decimal place.[1]

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
November, 1906.

INFLUENCE OF SOLVENTS IN THE CLAISEN CONDENSATION; CATALYTIC ACTION OF ETHER AND OF TERTIARY BASES IN THIS REACTION AND ALSO IN THE FORMATION OF THE GRIGNARD REAGENT.

(PRELIMINARY COMMUNICATION.)

BY J. BISHOP TINGLE AND ERNEST E. GORSLINE.

In a paper read in abstract before the American Chemical Society, at the New York meeting last December, we stated that we had obtained evidence which pointed to a specific action on the part of the solvent on the course of the Claisen condensation. We have now accumulated a number of observations bearing on this subject, all of which point to the *complete parallelism of the Claisen and Grignard reactions, so far as the effect of solvent is concerned.* We find that certain reactions, such for example as that between ethyl oxalate and camphor, take place readily and, apparently, with practically equal ease in ligroin or in ether solution. Others, such as that between ethyl phthalate and camphor, require many hours or days in ligroin solution, but take place easily when the materials are dissolved in ether. If a little ether be added to the ligroin solution, reaction begins at once and proceeds to completion. Apparently, the time required to carry the reaction to an end is dependent, other things being equal, on the amount of ether added. The position, then, is this, *we can accelerate or retard*

[1] Kohlrausch: Wied. Ann., **50**, 118 (1893); **53**, 15 (1894); **56**, 185 (1895).

a given condensation by adding or withholding ether from the solution.

The question at once arises, is this change in the velocity of the reaction due to a difference in the solvent action of the ether, or ether-ligroin mixture, as compared with the ligroin alone, or is it due to a difference of the temperature at which the reactions were carried out? With regard to the last point we may say that all our ligroin boiled at 36°, so that experiments carried out at its boiling point were practically at the same temperature as those carried out at the boiling point of ether. Actually, however, the majority of the experiments were performed at the temperature of the room. Moreover, we find that, under otherwise similar conditions, the time and temperature factors are inversely proportional, *i. e.*, a reaction which requires days for completion at the ordinary temperature, will be finished in a few hours if the temperature is raised to that of the boiling point of the solvent. The yield of the condensation product is practically the same in the two cases. In all our experiments, unless otherwise stated, we used sodium wire as the condensing agent. It is, perhaps, hardly necessary to add that, before use, all our solvents were treated with sodium wire until they ceased to react with it.

We may now take up the question of the solvent action of ether and ligroin. Camphor and all of the esters we employed dissolve in each solvent with great and, apparently, equal readiness, and the same is true of the condensation products, consequently the difference of solubility, if it exists, must be concerned with the sodium salts formed during the condensation of the ketone and ester. We have paid a good deal of attention to this point and have observed that the substances formed on the sodium wire sometimes flake off as rapidly as they are produced, and become partly suspended and partly dissolved in the liquid; often there is a deposit of this material on the bottom of the flask, frequently, however, it is all, or practically all, in solution. Sometimes the sodium wire becomes thickly incrusted with a hard, rough coating of a salt, which clings to the metal and retains the general shape of the original wire. Contrary to our expectations, the forma-

tion of this substance does not materially protect the sodium from being attacked by the reagents, nor does it adversely affect the yield of condensation product. Examination of the incrusted material will show that it often contains a minute thread of metal.

These differences appear to depend upon extremely subtle changes in temperature, speed of reaction, etc., and it is impossible for us to define exactly the conditions necessary for obtaining any given result, though all of them will be observed if a considerable number of condensations is carried out. In some instances, moreover, the sodium salt formed remains incrusted over the wire and retains the wire form when examination shows that all the sodium has disappeared. The interesting point in this connection is that the *yield of condensation product is essentially the same whether the sodium compound dissolves in the liquid, is suspended in it, or forms a crust over the sodium wire.* In order to cast a little additional light on the subject we prepared a concentrated solution of sodium ethylate in alcohol. Equal volumes of ether, ligroin, benzene and toluene were mixed with separate, equal quantities of this alcoholic solution; in no case was a precipitate or turbidity formed. As is well known, sodium ethylate free from alcohol is practically insoluble in ether or ligroin, but this fact has no direct bearing on our experiments. Having now determined the influence of all the factors which we thought likely to affect the result, and having established, thereby, the specific action of ether as an accelerator of the condensation, we turned our attention to the discovery of other substances which might exert a similar influence. Two of these we found to be pyridine and quinoline, which appear to be about equal in their efficiency. Their influence is quite well defined, though it is not as great as that of ether. We have carried out experiments in ligroin solution, adding a little of each tertiary base and have also made condensations with pyridine alone as the solvent. The results were similar in all cases. Furthermore, we believe that we have evidence showing that, in the case of condensation compounds capable of existing in both the enolic and the ketonic forms, the use of pyridine or quinoline

in the course of their formation leads to a disturbance of the ordinary equilibrium in favor of the production of the ketonic form. This is one of the points which is, at present, under investigation; should it prove to be substantiated we may expect that it will be of considerable importance in the preparation of the class of bodies in question.

One of the theories regarding the course of the Claisen condensation postulates the formation of sodium ethylate as the first step; this is supposed to undergo certain changes resulting, finally, in the elimination of 2 molecules of alcohol for each molecule of sodium ethylate added. In this manner it has been sought to explain the gradual acceleration of the reaction leading to the production of ethyl acetoacetate. Should this hypothesis be correct it is evident that sodium ethylate itself should be an excellent accelerator. This we have found to be the case. The addition of a few drops of absolute alcohol, saturated with sodium, to a mixture of ligroin, ethyl acetate and sodium wire immediately starts a reaction. A comparison experiment showed that alcohol itself assisted in promoting the action of the sodium, to an extent even greater than that exhibited by sodium ethylate. In presence of the latter the sodium wire was immediately darkened and the reaction continued steadily to the end. With the absolute alcohol the sodium wire remained entirely unattacked for nearly 5 minutes; a white compound was then formed in small quantity, and immediately thereafter a darker colored product. The reaction now proceeded rapidly and was apparently completed much sooner than when sodium ethylate was used. These experiments were carried out with camphor and ethyl phthalate, in ligroin solution. It may be added that in the course of a large number of experiments performed with various esters and condensing agents, we have never obtained a good yield of condensation product if we found it necessary to add alcohol in order to bring the sodium into solution. This is in entire accord with Claisen's experience. He found that sodium ethylate, in alcoholic solution, was the least active condensing agent. This point is at present under investigation.

In a series of papers of great interest, W. Tschelinzeff[1] has shown that the Grignard reagent is probably an oxonium derivative, that at all events, as usually prepared, it contains ether as an integral part of the molecule. He has also demonstrated that certain tertiary bases, such as dimethylaniline, can take the place of the ether and, further, that although, in the absence of ether or of a tertiary base, the formation of the Grignard reagent does not take place at the temperature of boiling ether, yet it does so if the temperature be sufficiently raised, say to that of boiling benzene or toluene. He points out that both the ether and tertiary base act as typical catalytic agents in this reaction, and gives the formulas $(C_2H_5)_2O\begin{matrix}\diagup MgR\\ \diagdown X\end{matrix}$ and $C_6H_5N(CH_3)_2\begin{matrix}X\\ |\\ MgR\end{matrix}$ as representing the probable constitution of the MgR ether compound and that of the tertiary base, respectively. It is at once evident that there is a close analogy between our results with the Claisen reaction and those of Tschelinzeff with the Grignard reagent. Accordingly, we have carried out a number of experiments to clear up certain points regarding which information was not available.

Our conclusions may be briefly summarized as follows: The rapidity with which the magnesium is attacked by the halide compound is dependent on the nature of the alkyl or aryl halide employed, provided, of course, that other conditions remain constant. The presence of ether is not essential to the reaction, *neither is a high temperature necessary, provided that sufficient time be allowed.* A number of our experiments were carried out at the ordinary room temperature, in ligroin solution (b. p. 36°). The Grignard reaction admits of being controlled with the greatest ease; as is well known, its velocity can be increased by the use of ether, a tertiary base (pyridine, quinoline, etc.), or iodine, or by means of a high temperature (see above). The use of low-boiling ligroin, on the other

[1] Ber. d. chem. Ges., **37**, 2081, 4534; **38**, 3664 (1905). Cf. Tingle: THIS JOURNAL, **38**, 94 (1906).

hand, quickly diminishes the speed of reaction. In short, then, we appear to have a *complete analogy in behavior between the Claisen reaction and the formation of the Grignard reagent.*

As regards the theory of the latter, we should like to offer a few remarks which will follow the same general lines as the ideas of Tschelinzeff, although there are one or two points which we think are not made quite clear in his paper. The reaction $Mg + RX \rightarrow Mg\langle^{R}_{X}$ takes place with more or less difficulty, depending on the factors referred to above. Grignard's reagent has the formula $Mg\langle^{R}_{X}$, *i. e.*, ether is *not* an essential constituent. The reaction represented above is greatly accelerated by the presence of a little ether, which acts as a catalyst, forming an oxonium compound such as $(C_2H_5)_2O\langle^{MgR}_{X}$ (Tschelinzeff). Evidently, however, this is *not* the compound which *necessarily* reacts with the aldehyde, ester, etc., in the Grignard condensations; although, of course, in presence of excess of ether it might be capable of doing so, it must, therefore, be an intermediate compound, in equilibrium, as represented by the equation: $Mg + RX + (C_2H_5)_2O \rightleftarrows (C_2H_5)_2O\langle^{MgR}_{X} \rightleftarrows (C_2H_5)_2O + Mg\langle^{R}_{X}$. The question now arises, to what is the acceleration of the ether due. As it is difficult to see how it can have any effect on the magnesium metal, we can only regard it as favoring the dissociation of the alkyl halide into R + X and, since the question is not one of dilution, we see no escape from the conclusion that it forms the oxonium compound, $(C_2H_5)_2O\langle^{R}_{X}$, which would certainly be unstable and would, therefore, in all probability, unite quickly with the magnesium to form $Mg\langle^{R}_{X}$. In support of

this theory of ours we may point out that the corresponding reaction with a tertiary base, leading, in the case of dimethyl-

aniline, to the production of the compound, $C_6H_5N\begin{matrix}(CH_3)_2\\ |\\ X\end{matrix}\!\!\begin{matrix}R\\ |\end{matrix}$, is exactly what we expect from such substances, whereas, to say the least, a compound, $C_6H_5N\begin{matrix}(CH_3)_2\\ |\\ X\end{matrix}\!\!\begin{matrix}MgR\\ |\end{matrix}$, as formulated by Tschelinzeff, is very unusual and without any special analogy. A further point for consideration is the effect of the trace of iodine which is so frequently added to start the attack on the magnesium. In view of the work of Baeyer and Villiger,[1] it can hardly be doubted that a magnesium subiodide, such as Mg_2I_2, is first produced and that this then reacts with the oxonium compound formulated above. Of course the magnesium is often attacked directly by the halide compound; to what extent this occurs obviously depends on the nature of the latter. To sum up, then, we regard the acceleration in the formation of the Grignard reagent as dependent on such actions as are represented by the equations:

(1) $Mg_2 + I_2 \rightarrow IMg.MgI.$

(2) $RX + (C_2H_5)_2O \rightleftharpoons \begin{matrix}C_2H_5\\ C_2H_5\end{matrix}\!\!\diagup\!\!O\!\!\diagdown\!\!\begin{matrix}R\\ X\end{matrix}$

(3) $(C_2H_5)_2O\!\!\begin{matrix}R + MgI\\ X\\ X\\ MgI\end{matrix}\!\!O(C_2H_5)_2 \rightarrow 2(C_2H_5)_2O + X_2 + 2RMgI.$

Almost ever since the discovery of ethyl acetoacetate the mechanism of its formation has been a matter of controversy. The investigation of the Claisen condensation, of which the

[1] Ber. d. chem. Ges., **36**, 2775 (1903). Cf. Tingle: THIS JOURNAL, **35**, 95 (1906).

reaction in question is a special case, so far from settling the matter, appeared to rouse the combatants to greater efforts and more vigorous language. During the past 10 years the dispute has been carried on chiefly by Claisen, Michael and Nef, each of whom had a particular theory to support. Quite recently Professor Nef has announced[1] that he has abandoned his own theory in favor of that of Claisen. It is but just to say that he is, apparently, at present, at least as emphatically in favor of Claisen's theory as, heretofore, he has been against it and that he now appears to be just as certain that Claisen is right and Michael is wrong as, in the past, he has been prepared to demonstrate, beyond question, that they were both absolutely in error. To us, and we believe to most chemists, the only thing about the matter which is beyond dispute is that when three investigators of the eminence of Messrs. Claisen, Michael and Nef disagree on a question, it may be taken as certain that the experimental data are necessarily inadequate to support any theory.

It would be easy for us to put forward a more or less attractive looking scheme of equations which could be made to include many fanciful dissociations and be in accord with our own work; we have not done so because we believe that such an attempt is premature in the present state of knowledge of the subject. Nevertheless, we desire to emphasize the fact that any hypothesis which may be put forward in the future will have to take account of the *accelerating action of ether and of the tertiary bases, and also of the similarity between the Claisen reaction and the formation of the Grignard reagent.*

EXPERIMENTAL.

The following experiments were carried out with camphor (1.5 mol.), unless otherwise stated. The proportion of sodium wire was 1 atom and of the particular ester 1 molecule.

1. No apparent action takes place on adding camphor, dissolved in ethyl benzoate, to sodium dissolved in absolute alcohol (4 mol.). After remaining for some hours the mixture was heated on the water-bath for 2 hours. A light colored

[1] THIS JOURNAL, 37, 302 (1907).

precipitate formed which gradually settled as a dark cake on the bottom of the vessel. Treatment with ice water, followed by acidification, gave unchanged ethyl benzoate. No condensation compound could be detected. This experiment shows how *slight* is the *condensing power of sodium ethylate*; the following 2 demonstrate the *effect of temperature.*

2. Ethyl benzoate and camphor, with sodium wire and ligroin (b. p. 36°), were mixed at the ordinary room temperature. After 48 hours, without heating, the sodium had almost entirely disappeared. In another experiment the time required was 5 working days.

3. In this experiment the mixture was heated on the water-bath to the boiling point of the solvent. After 2 hours action appeared to be complete, but the mixture was allowed to remain over night. The yield was practically the same as in 2.

Experiment 4 proves the effect of *differences in the ester.*

4. Ethyl oxalate, under conditions given in 2, reacts vigorously in a few minutes, without external heat. The yield was essentially the same as usual.[1]

The result of differences in the *constitution of the ketone or aldehyde* employed is sufficiently evident from Claisen's work, so that we paid no particular attention to this point.

Our next experiments were directed to prove that *the solvent* exercises a *decided effect on the progress of the reaction.*

5. Experiment 2 was repeated, except that to the 400 cc. of ligroin 100 cc. of absolute ether were added. The wire quickly darkened and became rough, and a dark mass collected at the bottom of the vessel. At the end of 3 hours, without heating, the action was complete and an excellent yield of condensation product was obtained. This, taken in conjunction with the second experiment, not only proves the question of acceleration, but also shows that the action is *not due* to *increased solubility* of any sodium salt in the ether-ligroin mixture, as compared with ligroin alone.

Experiments 6 and 7 demonstrate the result of the addition of *pyridine* and *quinoline*, respectively, in place of ether.

6. The conditions were similar to Expt. 5, but 75 cc. of

[1] *Vide* Bishop Tingle: THIS JOURNAL, **19**, 393 (1897); **20**, 218 (1898).

pyridine were added in place of the ether. The liquid rapidly darkened and behaved essentially as in the previous case. The reaction appeared to be complete in about 12 hours. The yield was poor.

7. In this case the pyridine was substituted by 20 cc. of quinoline. Action commenced at once, the liquid depositing a dark brown substance in the usual manner. The mixture was heated to boiling for 2 hours, at the end of which time the action was finished. The yield was good.

The influence of *sodium ethylate* or of *absolute alcohol, in small quantity*, is shown by Expts. 8 and 9.

8. Experiment 7 was repeated, but in place of the quinoline there was added 50 cc. of absolute alcohol saturated with sodium ethylate, *i. e.*, treated with the metal until the latter remained undissolved. The liquid darkened at once, the wire became coated and after 10 minutes the contents of the flask began to boil quietly. After 30 minutes the wire had completely disintegrated. The yield of condensation product was very poor, but a relatively large quantity of benzoic acid was obtained.

9. This was essentially the same as Expt. 8, except that for the sodium ethylate solution there was substituted an equal volume of absolute alcohol. The action was complete in 15 minutes and, as in the previous case, a red mass settled to the bottom of the vessel.

We have carried out experiments with camphor and ethyl phthalate similar to Expts. 2, 5, 7, 8 and 9 recorded above for ethyl benzoate. In general, the results were entirely analogous; the chief difference is that ethyl phthalate reacts rather more readily than ethyl benzoate. In a further experiment we tried the effect of adding 2 drops of sodium ethylate solution, as above, to the substances dissolved in 200 cc. of ligroin. The reaction was, of course, not so rapid as in those experiments where a larger quantity was added, but its accelerating action was more marked than that of 10 cc. of quinoline or 25 cc. of ether, under similar conditions. The yield was, however, *markedly less*, only about half of that obtained by the use of ether or of quinoline, or when no accelerator is employed.

We have also studied the condensation of ethyl acetate to ethyl acetoacetate. By dissolving the ester (17.6 grams) in ligroin (b. p. 36°, 200 cc.) and adding the sodium wire, the reaction proceeds very slowly and was not completed after 6 hours' boiling; indeed, some wire remained undissolved after 5 days' subsequent standing, at the ordinary temperature. In contrast with this the addition of 75 cc. of ether caused the disappearance of the sodium after 2 hours' heating. Pyridine (50 cc.) acted in almost exactly the same way. The use of 5 drops of sodium ethylate solution once more demonstrated how rapidly this substance stimulates a reaction. After 0.5 hour at the ordinary temperature and 1 hour's heating, the sodium had nearly all dissolved. The ethyl acetoacetate was separated and identified in the usual manner, by the ferric chloride test and by fractionation under reduced pressure.

EXPERIMENTS ON GRIGNARD'S REACTION.

Ethyl chloracetate, in ethereal solution, reacts very vigorously with magnesium. In ligroin (b. p. 36°) solution, on the other hand, no change was apparent after 3 hours' boiling. The addition of a fragment of iodine, followed by boiling for 10 hours, caused the production of a quantity of light yellow material. The experiment was repeated, 10 cc. of ether being used in addition to the ligroin. There was no change after 3 hours' boiling, but when a fragment of iodine was added a rather vigorous action began, the light yellow solid collecting in fairly considerable quantity. This demonstrates the *formation of Grignard's reaction at 36°.*

Experiments were now carried out with ethyl iodide (7.8 grams), magnesium (1.22 grams), ligroin (500 cc.) and quinoline (30 cc.). There was no evident action on standing at the ordinary room temperature, but the magnesium was almost completely dissolved after boiling during 20 minutes. The experiment was repeated, ether (25 cc.) being substituted for the quinoline. In this case the reaction began vigorously in the cold and the liquid soon commenced to boil.

Further experiments were carried out with pyridine in the

place of quinoline, the results being essentially similar to those described above.

Our work is being continued in several directions and we hope to communicate further results, together with fuller experimental details, in a subsequent paper.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MARYLAND,
April, 1907.

Contributions from the Sheffield Laboratory of Yale University.

ON THE MOLECULAR CONDITION OF SALTS DISSOLVED IN A FUSED SALT.

BY H. W. FOOTE AND L. H. LEVY.

The lowering in the freezing point of a fused salt, caused by comparatively large percentages of a second salt, has been determined in a great many cases. The accurate determination of the lowering in freezing point of a salt caused by the addition of small amounts of another, has been difficult on account of the high melting points of most salts. It has seemed to us, however, that just such a determination would have some interest as we might expect the laws for dilute solutions to apply in this case. For this reason we have undertaken to determine accurately the lowering in the freezing point of sodium chlorate, caused by small amounts of other salts in solution.

The melting point of sodium chlorate is only 255°. Differences in temperature at this melting point can be determined with a considerable degree of accuracy with the ordinary Beckmann thermometer, as we have convinced ourselves by many experiments. The salt can be obtained in very pure condition indeed, it is a good solvent for other salts and its tendency to supercool without freezing is very slight. This salt appeared, on the whole, to be the best for our purposes and it has been used as a solvent in our experiments.

From the experimental data which are given below we have calculated the molecular weights of a considerable number of salts containing a radical in common with sodium chlorate. The results are discussed later.

The molecular weights were calculated from the well-known formula,

$$M = \frac{ks}{\Delta L},$$

in which M = the molecular weight, s = the weight of dissolved substance, Δ = the lowering in the freezing point of the solvent, L = the weight of the solvent, and k is the constant for sodium chlorate. To obtain the constant k, the heat of fusion of sodium chlorate was determined. The constant was then calculated from the van't Hoff formula,

$$k = \frac{2T^2}{\lambda},$$

in which T = the absolute melting point and λ the heat of fusion in calories of 1 gram of sodium chlorate. The heat of fusion was calculated from determinations of the amount of heat evolved by sodium chlorate in a water calorimeter when this salt had been heated at 2 temperatures above the melting point and at 2 temperatures below. The specific heats of sodium chlorate slightly above and below the melting point could be calculated by this method and the heat of fusion determined from the formula:

$$\lambda = Q - c_1(t_a - t_s) - c_2(t_s - t_b) - H.^1$$

In this formula,

λ = heat of fusion of 1 gram sodium chlorate.

t_a, t_b = respectively, temperatures slightly above and below the melting points of sodium chlorate.

t_s = melting point of sodium chlorate, 255.°.

c_1, c_2 = respectively, the specific heats of liquid and solid sodium chlorate near the melting point.

Q = heat evolved by 1 gram of sodium chlorate cooled from temperature t_a to 22°.

H = heat evolved by 1 gram of sodium chlorate cooled from temperature t_b to 22°.

For the determinations, fused sodium chlorate, which had been recrystallized, was poured into capsules holding 50–60

[1] Cf. Ostwald-Luther: Physico-Chem. Messungen, p. 206.

grams. The capsules were made of brass, silver, or platinum, and the results were practically independent of the metal used in the capsule after a correction was introduced for the heat evolved by the metal. The cover to the capsule was not quite water-tight, so the joint was covered, while the capsule was hot, with linseed oil which had been boiled till it was very thick. This made a hard enamel on cooling and made the brass capsule perfectly tight. The other capsules always admitted a small amount of water when cooled in the calorimeter, but the very small error introduced here, due to the heat of solution, could be disregarded. The capsules, filled with a weighed quantity of sodium chlorate, were heated at the temperature desired for 2 hours or more, in a glass tube which was kept in a low-fusing bath whose temperature could be kept constant within 1°. This bath was made of about equal parts of sodium and potassium nitrates and sodium nitrite. It fused below 200° and served its purpose admirably here as well as in the determination of the lowering of the melting point. The bath was fused in a "granite-ware" kettle and was stirred continuously during an experiment. When the capsules were to be heated above the melting point of sodium chlorate, the temperature was raised at first considerably higher than the temperature desired, to be sure of complete melting, and then it was lowered to the point required. After heating, the capsule was removed quickly from the heating tube and plunged in the calorimeter. The operation required not more than 1 or 2 seconds. The calorimeter was a large one, kindly loaned us by Prof. W. G. Mixter, who has already described it.[1] It had a heat capacity of 50 calories and held about 3 kilos of water. The amount of water used was determined by weighing on a balance, which weighed several kilos with an error of a few milligrams. The temperature of the calorimeter was adjusted before each experiment so that the temperature, after the capsule was introduced, should be approximately 22°. The calorimeter was stirred with a small screw propeller, which was driven by a water-motor running with compressed air. A series of readings was taken

[1] Amer. J. Sci., 16, 214.

before and after the capsule was introduced and the corrected difference in temperature extrapolated in the usual manner. The heat evolved by the empty capsules was determined by experiment instead of calculating this value from the known specific heats.

The heat evolved by 1 gram of sodium chlorate, cooling from the temperature t to 22°, was calculated from the expression,

$$\frac{h\Delta - R}{L},$$

where h = the heat capacity of the calorimeter and water contained in it.

Δ = rise in temperature of the water.

R = heat evolved by the metal capsule containing the chlorate.

L = weight of chlorate.

In the following table the experimental data are given, together with the calculated result for the heat evolved by 1 gram of sodium chlorate:

Table I.

Capsule.	Temp.	h.	Δ.	R.	L.	Heat evolved.
Brass No. 1	272	2852	2.443	1267	48.2	118.5
Platinum	268	2814	2.276	214	52.5	117.9
Brass No. 1	259	2954	2.226	1202	48.2	111.5
" No. 2	259	2980	2.318	1331	49.7	112.2
Platinum	246.5	2997	1.266	195	61.3	58.7
Silver	246.5	2990	1.312	530	57.5	59.0
Platinum	246.5	2987	1.291	195	62.4	58.7
Silver	246.5	3000	1.285	530	56.5	58.8
Brass No. 2	221	2856	1.248	1006	49.7	51.5
" No. 1	220.5	2852	1.219	991	48.2	51.6
Silver	220.5	3014	1.171	466	59.7	51.3

The specific heats, c_1 and c_2, of liquid and solid sodium chlorate are readily calculated from the results in the last column. They are:

$$c_1 = 0.581,$$

$$c_2 = 0.281.$$

The heat of fusion can now be calculated from the formula previously given:

$\lambda = 111.85 - 0.581(259° - 255°) - 0.281(255° - 246.5) - 58.5;$

$\lambda = 48.4$ *calories.*

Substituting this value in the van't Hoff formula,

$$k = \frac{2T^2}{\lambda},$$

$$k = \frac{2 \times (528)^2}{48.4} = 11500.$$

The Beckmann freezing point apparatus, with some modifications to fit our conditions, was used to determine the lowering of the freezing point. The freezing bath consisted of the same mixture of sodium and potassium nitrates and sodium nitrite which was used in determining the heat of fusion of sodium chlorate. The bath was held at 249°–250° by regulating the gas supply and stirring the mixture thoroughly. The bath weighed several kilos, so that the temperature changed but slowly, and it was an easy matter to hold it nearly constant. The outer freezing jacket of the Beckmann apparatus dipped into the bath, and the inner freezing tube containing the chlorate, fitted into the jacket, leaving an air space between. A second smaller bath was heated considerably above the melting point of sodium chlorate and was used to melt the chlorate before the freezing point determination was made.

Assuming that the value of a degree, as registered by a Beckmann thermometer, is correct for 20° C., the value is too small for higher temperatures, since mercury is removed from the bulb and not as much mercury is left to expand. The correction is very small for ordinary boiling and freezing point determinations and is usually neglected. At 255°, however, the freezing point of sodium chlorate, this error is not negligible and we have introduced a correction. If q represents the value of 1° on the Beckman thermometer, at 250°, compared with the value at 20°, and α represents the coefficient of expansion of mercury in glass,

$$\text{then } q = \frac{1 + 20\,\alpha}{1 + 250\,\alpha}.$$

For α we have used the value 0.000157, so that

$$q = 0^{\circ}.965.$$

The observed lowering of the freezing point of sodium chlorate has been corrected throughout by dividing by this value, 0.965.[1]

For each experiment, about 30 grams of sodium chlorate in a freezing tube were placed in the melting bath until the salt fused to a clear liquid. The tube was then transferred quickly to the freezing bath and the freezing point determined. Every freezing point was determined 2 or 3 times, the chlorate being completely melted between each reading. Duplicate readings on the pure chlorate and on the solutions seldom differed from each other more than 0°.01. Weighed quantities of salt were added to the chlorate, dissolved by thorough stirring and the freezing point determined after each addition.

Fused sodium chlorate shows a slight tendency to supercool. By stirring regularly before the freezing point was reached the supercooling did not exceed 0°.2–0°.3 and the temperature rose quickly to the freezing point when freezing began. No correction was applied for the additional concentration of the solution due to the separation of the solid.

The molecular weight was calculated from the formula given previously,

$$M = \frac{ks}{\Delta L}.$$

Every series of determinations was duplicated. Several sodium salts could not be used. Sodium sulphate and tetraborate were too insoluble. Sodium iodide and dichromate decomposed in the melted chlorate. Of the salts which were used, sodium fluoride and chloride were difficultly soluble, the fluoride especially so. The results are given in the following table. The theoretical molecular weight is put in parenthesis after the formula of the compound. The symbols at the

[1] Ostwald-Luther: Phys. Chem. Meas., p. 291.

head of the columns are those used in the molecular weight formula:

Table II.

L.	s.	Grams solute in 1000 grams solvent.	Δ.	M.
		NaCl (58.5).		
28.544	0.0832	2.92	0.534	63
"	0.2481	8.69	1.570	64
30.215	0.1478	4.89	0.833	67.5
"	0.2561	8.48	1.473	66
		$NaNO_3$ (85).		
32.393	0.1625	5.33	0.637	91
"	0.2899	8.95	1.124	92
37.393	0.9629	25.75	3.062	97
30.300	0.2026	6.69	0.855	90
"	0.4063	13.41	1.696	91
"	0.7024	23.18	2.893	92
		NaBr (103).		
29.565	0.3000	10.15	1.129	103
"	0.8051	27.23	2.980	105
30.000	0.4002	13.36	1.461	105
"	0.6614	22.06	2.401	105
"	1.1945	39.82	4.238	108
		Na_2CO_3 (106).		
30.025	0.0340	1.13	0.107	121
"	0.1113	3.71	0.355	120
"	0.3503	11.66	1.133	118
30.195	0.0543	1.80	0.183	113
"	0.3074	10.18	1.043	112
40.195	0.6209	15.45	1.673	106
		Na_2CrO_4 (162).		
30.120	0.1605	5.33	0.379	162
"	0.3766	12.50	0.890	162
"	1.2298	40.84	2.790	168
30.305	0.2310	6.05	0.541	162
"	0.3736	12.34	0.873	162
		NaF (42).		
30.615	0.1253	4.09	1.078	44
"	0.1926	6.29	1.501	48
30.040	0.1093	3.64	0.935	45

Table II (Continued).

$KClO_3$ (122.6).

L.	s.	Grams solute in 1000 grams solvent.	Δ.	M.
29.981	0.1742	5.81	0.497	134
"	0.5455	18.19	1.565	134
"	0.9002	30.03	2.591	133
30.185	0.421	13.94	1.209	132
"	1.1898	39.42	3.330	136
"	1.3770	45.62	3.857	136

$CsClO_3$ (216).

30.240	0.2290	7.57	0.403	216
"	0.6893	22.79	1.225	214
30.595	0.2430	7.94	0.427	214
"	0.7266	23.75	1.305	209

$Ba(ClO_3)_2$ (304.4).

29.828	0.6962	23.34	0.839	320
"	1.2639	42.37	1.523	320
"	1.7641	59.15	2.104	323
30.280	0.6289	20.77	0.765	312
"	1.3296	45.87	1.595	317
"	3.2069	105.66	3.819	319

Taken as a whole, the results show very nearly normal molecular weights. In every case but one the molecular weights are slightly higher than the calculated values. While this may be due to slight polymerization, or, especially in the case of potassium chlorate, to a slight tendency to form mixed crystals, we are inclined to believe that the high values are due either to a small error in determining the heat of fusion, which would affect the value of the constant in the molecular weight formula, or to the fact that the gas laws do not hold with great accuracy in the solutions. The determination of the heat of fusion was not by any means a simple matter. The results, we believe, prove that *salts dissolved in fused sodium chlorate show no appreciable tendency toward polymerization.*

On the other hand, although the molecular weights calculated indicate no dissociation, the results can equally well be explained by assuming that dissociation is present. If pure

fused sodium chlorate is partially dissociated, the ions should lower the freezing-point, so that the pure salt would melt at a lower temperature than it would if there were no dissociation. When a salt is added with a common ion, assuming that it is largely dissociated, it would tend to repress the dissociation of the sodium chlorate, thus raising the melting point. At the same time its ions would lower the melting point and the joint effect would be the same as though neither were dissociated. This can be shown very simply in the following manner: Let x gram-equivalents of a sodium salt, such as sodium nitrate, be added to a unit volume of sodium chlorate. Assuming no dissociation, the concentration of the dissolved molecules would be x. On the other hand, let x gram-equivalents of sodium nitrate be added to the unit volume of sodium chlorate, assuming the former to be completely dissociated and the latter partially so. In the pure chlorate, if c_o represents the concentration of the sodium and the chlorate ions, by the law of mass action,

$$c_o^2 = K. \tag{1}$$

When x gram-equivalents of sodium nitrate are added, the concentrations of the sodium and chlorate ions originally present change to new values which may be represented by $c_o^1 + x$ and c_o^1, respectively, and since the product of the ions must remain constant,

$$(c_o^1 + x)c_o^1 = c_o^2. \tag{2}$$

If the dissociation of sodium chlorate is moderately large, x is small compared to c_o^1 and equation (2) may be simplified to

$$c_o^1 + \frac{x}{2} = c_o,$$

or

$$c_o^1 = c_o - \frac{x}{2}. \tag{3}$$

The total concentration of ions after x gram-equivalents of sodium nitrate were added would be:

$$\underset{\text{Na ions}}{c_o^1} + x + \underset{\text{ClO}_3\text{ ions}}{c_o^1} + \underset{\text{NO}_3\text{ ions}}{x},$$

or the total concentration of ions becomes

$$2c_o^1 + 2x. \tag{4}$$

Substituting the value of c_o^1 from (3) in (4) the total concentration of ions becomes

$$2c_o - x + 2x,$$

or

$$2c_o + x.$$

Since the original concentration of ions was $2c_o$, it follows that the concentration of ions in the sodium chlorate has increased by x, although $2x$ ions were added. It follows that *the increase in the number of ions present, caused by adding x equivalents of a completely dissociated salt with a common ion, would be equal to the number of molecules added by x equivalents of an undissociated salt.* The depression of the freezing point would thus be the same in either case and our results give no positive information as to whether or not the dissolved salts are largely dissociated.

In the demonstration as outlined above, it was assumed that the dissolved salt was very largely or completely dissociated and that the dissociation of sodium chlorate was considerable. If the dissociation of sodium chlorate were very slight, the depression of the freezing point would be greater when the dissolved salt was dissociated than it would be if undissociated. This is the case with solutions in water, as is well known.

An experiment was tried to show that both solvent and solute could not be very largely dissociated by comparing the depression of the freezing point caused by potassium nitrate or potassium chloride with that of sodium nitrate, the latter containing an ion in common with sodium chlorate. If neither solvent nor solute dissociate, the reaction

$$NaClO_3 + KNO_3 = NaNO_3 + KClO_3$$

should be very nearly complete when potassium nitrate is dissolved in an excess of sodium chlorate, on account of the

mass action of an excess of sodium chlorate. For every molecule of potassium nitrate added, therefore, 2 other molecules are formed. By dissolving an equivalent amount of sodium nitrate in sodium chlorate double decomposition is impossible, so that the lowering of the freezing point in the first case should be double that in the second. If both solvent and solute were largely or completely dissociated there would be no chance for reaction in either case, as may be seen if we write the substances in the form of ions:

$$Na + ClO_3 + K + NO_3;$$
$$Na + ClO_3 + Na + NO_3.$$

The depression should, therefore, be the same whether sodium or potassium nitrates were used in equivalent amounts. To obtain comparative results between the lowering caused by sodium nitrate and that caused by potassium nitrate, or potassium chloride, we have recalculated our previous results on sodium nitrate to obtain the molecular weight constant, assuming the molecular weight of sodium nitrate to be normal. The result was

$$k = 10700.$$

Using this value, the lowering produced by potassium nitrate or potassium chloride could be calculated in case it behaved like sodium nitrate, and this calculated lowering could be compared with that actually observed. The results obtained were as follows:

L.	*s.*	Δ observed.	Δ calculated.	$\frac{\Delta \text{ observed}}{\Delta \text{ calculated}}$.
		KNO_3.		
29.935	0.2730	1.922	0.963	1.996
"	0.4363	3.062	1.544	1.983
30.430	0.2210	1.579	0.770	2.05
"	0.4325	2.982	1.506	1.987
		KCl.		
30.010	0.1981	1.777	0.927	1.91
30.205	0.3084	2.792	1.904	1.90

From the ratios in the last column it will be noticed that the observed depression in each case is nearly twice the depression that would be caused if equivalent amounts of sodium

nitrate were used. This would indicate that neither solvent nor solute were dissociated, instead of both being largely or completely so. The results can, however, be explained by assuming that the solute is largely dissociated and the solvent less so, by a method similar to that used previously in showing that dissolved substances may be dissociated, although the molecular weights calculated are normal.

The molecular weights of a number of chlorides and bismuth salts, dissolved in bismuth chloride, have been determined by Rügheimer[1] from vapor pressure measurements on bismuth chloride. The only salt whose molecular weight has been determined by both of us is sodium chloride. The average value found by him was 65, which is also the average of our results. The same objection may be raised to his results that we have mentioned in regard to ours, that the solvent may be somewhat dissociated and the solute largely so. The addition of the dissociated solute would repress the dissociation of the solvent, tending to raise the vapor pressure, while the ions added have the opposite effect, the result being that the vapor pressure is lowered as it would be if the molecular weight of the solute were normal.

Silver chlorate, as is well known, forms mixed crystals readily with sodium chlorate.[2] It would be expected, therefore, that when the solvent separated it would carry a certain proportion of solute with it, so that the observed depression of the freezing point would be too low and the molecular weight calculated would be high. The determinations which follow show this to be the case.

$AgClO_3$ (191.5).

L.	*s.*	Grams solute in 1000 grams solvent.	Δ.	M.
30.390	0.6222	20.47	0.346	680
"	0.9295	30.58	0.524	671
30.295	0.9316	30.75	0.529	669
"	1.5766	52.05	0.888	674
"	3.1449	103.8	1.720	694
"	6.2676	206.9	3.287	724
"	7.8656	259.6	4.060	735

[1] Ann. Chem. (Liebig), **339**, 297.

[2] Z. physik. Chem., **5**, 438 (1890). THIS JOURNAL, **27**, 345 (1902).

We hope, later, to attack the problem of molecular weights in fused sodium chlorate from another side.

We wish to express our sincere thanks to Prof. W. Nernst for some very valuable criticisms and suggestions in connection with this work.

Summary.

In the present article the heat of fusion of sodium chlorate has been determined and the constant for sodium chlorate calculated in the molecular weight formula,

$$M = \frac{ks}{\Delta L}.$$

The lowering in the freezing point of sodium chlorate produced by small amounts of other salts has been determined with considerable accuracy.

The molecular weights of a number of chlorates and sodium salts have been calculated from the data obtained and found to be nearly normal.

The results indicate that there is little or no polymerization, but they do not prove that dissociation is absent, as nearly normal molecular weights would be obtained if the solute were very largely dissociated and the solvent somewhat less so.

NEW HAVEN, CONN.,
December, 1906.

Contributions from the Chemical Laboratory of the University of Illinois.

ON REVERSIBLE METALLIC DISPLACEMENTS IN AQUEOUS SOLUTIONS.

BY GEORGE MCPHAIL SMITH.

INTRODUCTION.

When a metal is immersed in the solution of an electrolyte, the solution pressure of the metal tends to drive particles of it into the solution. These particles, or ions, carry positive electric charges, from which it results that the solution becomes positively charged, and the metal negatively charged. These charges give rise to a force component, which, on the one hand tends to prevent the entrance of more metallic ions in the solu-

tion, and on the other hand seeks to drive positive ions from the solution back to the metal. If the solution pressure of the metal is sufficiently high, ions of it continue to be driven into the solution, and, at the same time, the electrically equivalent quantity of other positive ions are forced in the opposite direction from the solution to the metal. Here they give up their charges and separate in the free state. This is the process which takes place, for example, when copper is precipitated from its salt solutions by zinc, or when water is decomposed by sodium.

In general, according to Nernst, to whom we owe the above conceptions, when one metal is immersed in the solution of a salt of another metal, the relation

$$\sqrt[n_1]{\frac{P_1}{p_1}} > \sqrt[n_2]{\frac{P_2}{p_2}}$$

must hold, in order that the second metal may be precipitated by the first. In this formula the index 1 refers to the first metal and 2 to the second metal; P_1 and P_2 are the electrolytic solution pressures, p_1 and p_2 the osmotic pressures of the ions, and n_1 and n_2 the valencies of the metals in question.

As a necessary consequence of this, it follows, that of any 2 metals, either can be made to displace the other from a solution, provided that the relative magnitudes of

$$\sqrt[n_1]{\frac{P_1}{p_1}} \text{ and } \sqrt[n_2]{\frac{P_2}{p_2}}$$

can be reversed under different conditions. Whether hydrogen will be evolved or not will depend on the relative magnitudes of

$$\frac{P_H}{p_H} \text{ and } \sqrt[n]{\frac{P_M}{p_M}},$$

where H refers to hydrogen and M to any metal present as such. That these conclusions are in harmony with the facts in a number of cases has been previously shown by the author.[1]

[1] J. Am. Chem. Soc., **27**, 540 (1905).

I.

THE ACTION OF THE AMALGAMS OF THE ALKALI AND ALKALI EARTH METALS ON VARIOUS AQUEOUS SOLUTIONS.

Previous Work.

As early as 1834, R. Boettger[1] prepared dilute amalgams of barium and strontium by the action of saturated solutions of their chlorides on sodium amalgam. It has since been established that this method is generally applicable for the preparation of the amalgams of metals which are more electronegative than sodium.

In 1871, Kraut and Popp[2] found that a crystalline potassium amalgam was formed when sodium amalgam was allowed to stand for several days under a strong solution of potassium hydroxide or carbonate. This displacement of potassium by sodium was long regarded as an anomaly, and Berthelot and others[3] have explained it as the necessary consequence of the greater loss of energy undergone by potassium than by sodium in the formation of their respective amalgams. That sodium might, in like manner, be displaced from its solutions by potassium does not appear to have entered their thoughts.

In 1903, G. Fernekes[4] investigated the action of sodium and potassium amalgams on various aqueous solutions. He found that solutions of sodium, potassium, barium and certain other chlorides, for example, when acted upon by sodium or potassium amalgam, evolved hydrogen more slowly than pure water. Further, he found that the retardation of the rate of liberation of hydrogen by sodium or potassium amalgam was about the same for isotonic solutions of sodium chloride and potassium chloride. He thought the theory of electrolytic dissociation was out of harmony with these results and, in his eagerness to find that theory at fault, he overlooked the obvious explanation.

In the same year, Kettembeil[5] prepared sodium amalgam

[1] J. prakt. Chem., 1, 302 (1834).
[2] Ann. Chem. (Liebig), 159, 188 (1871).
[3] Ann. Chim. Phys. [5], 18, 442 (1879). Kerp: Z. anorg. Chem., 17, 296 (1898).
[4] Disser'n. Univ. Wisconsin; J. Physic. Chem., 7, 611 (1903).
[5] Z. anorg. Chem., 38, 227 (1904).

by means of potassium amalgam, as follows: The electrolytes in 2 vessels, the one containing potassium amalgam under a solution of potassium hydroxide, and the other mercury, immersed in a solution of sodium hydroxide, were brought into contact by means of an inverted U-tube. The mercury, which was suspended in the sodium hydroxide solution, was then connected with the potassium amalgam in the first vessel by means of outside wires. After a few minutes the mercury was lifted out of the solution, quickly washed and then brought into contact with a strong solution of ammonium chloride. This gave rise to the formation of the characteristic ammonium amalgam, and thus proved the presence of sodium in the mercury.

Finally, in 1904, and independently of Kettembeil, it was shown by the author[1] that in the case of sodium and potassium either can be directly replaced by the other in its amalgam, by simply treating the amalgam in question with a solution of the chloride of the other metal. In a later paper[2] it was further shown that amalgams containing potassium or sodium can be obtained readily from barium amalgam by treating it with a concentrated solution of potassium or sodium hydroxide.

Constitution of the Amalgams.

In the case of the metals of the alkali and alkali earth groups, with which the present paper deals, it is practically impossible to work with the metals themselves in the presence of water. For that reason the amalgams of these metals were employed. At first, in accordance with the generally accepted view, it was supposed that, in mercurial solution, these metals existed as such, in the monatomic condition. This idea was abandoned, however, early in the course of the present work.

Recent investigators are unanimous in regarding the solid, crystalline amalgams of the alkali and alkali earth metals as

[1] J. Physic. Chem., 8, 566 (1904).
[2] *Ibid.*, 9, 13 (1905).

definite chemical compounds.[1] The corresponding liquid amalgams, on the other hand, have generally been regarded as mercurial solutions of these metals in the monatomic condition.[2] This view appeared all the more reasonable because it agreed remarkably well with what was known of the metals in the gaseous state. It is the view still expressed in the latest books on physical chemistry.[3] In a preliminary communication, however, it has been shown by the author that this view is without experimental foundation; the experimental data point rather to the conclusion that the liquid amalgams of the alkali and alkali earth metals are solutions in mercury of compounds of the general formula MHg_m, containing only 1 atom of the amalgamated metal to the molecule. This conclusion is further borne out by the results obtained in the present investigation.

According to the work of Kerp and Böttger,[5] who applied the phase rule to solutions of these metals in mercury, the solid amalgams appear to have the following compositions:

KHg_{12}, from 0°–71°; above 71° the solid phase becomes richer in alkali metal.

$NaHg_6$, from 0°–40°.5; $NaHg_8$ from 40°.5 – ±150°.

$LiHg_8$, from 0°–100°.

$SrHg_{12}$, from 0°–30°; above 30° the solid phase becomes richer in strontium. According to Guntz and Roederer,[6] however, this amalgam has the composition indicated by $SrHg_{11}$.

$BaHg_{13}$, from 0°–30°; $BaHg_{12}$, from 30°–100°.

[1] Berthelot: *Loc. cit.* Kerp: Z. anorg. Chem., **17**, 284 (1898). Kerp and Böttger: *Ibid.*, **25**, 1 (1900). Maey: Z. physik. Chem., **29**, 119 (1899). Guntz and Ferée: Compt. rend., **131**, 182 (1900). Kurnakoff: Z. anorg. Chem., **23**, 439 (1900). Haber and Sack: Z. Elek. Chem., **8**, 245 (1902).

[2] Ramsay: J. Chem. Soc., **55**, 521 (1889). Heycock and Neville: *Ibid.*, **53**, 666 (1889); **57**, 376 (1890). Tammann: Z. physik. Chem., **3**, 441 (1889). G. Meyer: *Ibid.*, **7**, 447 (1891). Kerp: Z. anorg. Chem., **17**, 286 f. (1898). Schoeller: Z. Elek. Chem., **5**, 259 (1898). Erdmann: Z. anorg. Chem., **32**, 404 (1902). Rich and Travers: J. Chem. Soc., **89**, 872 (1906).

[3] Ostwald: "Lehrbuch," I., pp. 737, 767; II., pp. 859, 862 (1903).

[4] THIS JOURNAL, **36**, 124 (1906).

[5] *Loc. cit.*

[6] Bull. Soc. Chim. [3], **35**, 494 (1906).

The liquid phases corresponding to saturated solutions of these metals in mercury were found to contain:

Temperature.	K. Per cent.	Na. Per cent.	Li. Per cent.	Ba. Per cent.	Sr. Per cent.
0°	0.31	0.53	0.04	0.15	0.73
20°	0.47	....	.....	0.32	1.02
25°	0.53	0.65	....	0.34	.....
64°.5	....	....	0.10	....	....

The solid amalgams are to be regarded as analogous to hydrated salts, *i. e.*, as being made up of a fundamental compound of mercury and alkali, or alkali earth metal, combined with various amounts of "mercury of crystallization."[1] The liquid amalgams are solutions of the solid amalgams in mercury.

Although each of the amalgams mentioned above is a definite compound of mercury with another metal, they are, nevertheless, all slowly decomposed by water, with the evolution of hydrogen and the simultaneous formation of the corresponding metallic hydroxides. The amalgamated metal, owing possibly to a partial dissociation of its mercury compound, has a certain tendency to enter the solution in the ionic condition, *i. e.*, it possesses a certain electrolytic solution pressure, and the introductory considerations may be applied to it just as if it were present in the mercury in the atomic condition.

EXPERIMENTAL PART.

Preparation of the Amalgams.

The mercury used in the preparation of these amalgams was purified as follows: First it was shaken with a dilute solution of potassium dichromate, which was acidified with sulphuric acid; it was then allowed to run in a finely divided state from the capillary end of a funnel, into a solution of 75 grams of mercuric nitrate and 75 cc. of nitric acid, sp. gr. 1.42, in 800 cc. of water. This solution was contained in an upright glass cylinder, 1.3 meters in height, such as is commonly used for the purpose. The mercury was allowed to fall through this solution several times in succession, and its purity was finally confirmed by analysis.

[1] Berthelot, Kerp, Böttger, Kurnakoff and Maey: *Loc. cit.*

Potassium Amalgam.—This amalgam was prepared by the addition of 7 grams of potassium, in small portions, to 500 grams of mercury, which had previously been heated on the water-bath. After cooling, the amalgam was washed, dried with filter paper, and bottled. It should be kept in a small, tightly-stoppered bottle, because, in contact with a limited quantity of air, especially in a large bottle which is occasionally opened, the amalgam becomes coated with a dark layer of potassium suboxide,[1] mixed with finely divided mercury. After this has happened, the amalgam decomposes water with stormy violence and cannot be used for the following experiments. The pure amalgam decomposes water at a very moderate rate.

Sodium Amalgam.—This amalgam was prepared by adding 15 grams of sodium, in small quantities, to 1 kilo of mercury, at the ordinary temperature. The action was, in this case, very violent and the temperature rose to above 150°. After cooling, the amalgam was kneaded under water until thoroughly clean. It was then dried with filter paper and bottled. Sodium amalgam, when exposed to the action of a limited quantity of air, does not behave like potassium amalgam. It becomes coated with a thin, white deposit, but its action on water is not altered.

Lithium Amalgam.—This amalgam was also prepared directly from the elements. The lithium was obtained from Kahlbaum, and it was previously analyzed; 0.2 gram of the metal gave 0.0052 gram potassium chlorplatinate, equivalent to 0.0008 gram of potassium, and the filtrate from this, after evaporation, gave a faint sodium spectrum which did not last 3 seconds. The lithium was, therefore, exceptionally pure.

Two grams of lithium and 500 grams of mercury were heated together in a small flask at 220°, in a paraffin bath. On stirring, the mixture exploded and the flask was shattered. Most of the amalgam, however, fell into the bath, where it was protected from oxidation by the paraffin. It was removed after cooling and bottled. Analysis:

100 grams of the amalgam gave Li_2SO_4 0.2974 gram.

[1] Cf. Moissan: "Traité de Chimie Minérale," III., 70.

It contained, therefore, 0.038 per cent of lithium.

Lithium amalgam decomposes water more rapidly than either sodium or potassium amalgam. It is also much less stable in the presence of air.

Barium Amalgam.—This amalgam was prepared by stirring 500 grams of sodium amalgam, for periods of 5 minutes, with 5 successive portions, of 50 cc. each, of saturated barium chloride solution, at 90°. The amalgam was then shaken for a few seconds with very dilute hydrochloric acid. Finally, it was allowed to stand for 5 hours, with occasional shaking, under a strong solution of barium chloride, containing a little barium hydroxide. The resulting amalgam was diluted with mercury. Analysis:

50 grams of the product gave $BaSO_4$ 0.7835 gram and Na_2SO_4 0.0032 gram.

It therefore contained 0.922 per cent of barium and 0.002 per cent of sodium.

Strontium Amalgam.—This amalgam was prepared by treating 500 grams of sodium amalgam, at 85°, for periods of 2 minutes, with 4 separate portions, of 25 cc. each, of saturated strontium chloride solution. The amalgam was then washed, and shaken for 2 minutes with hot water. Analysis:

50 grams of the amalgam gave 0.1418 gram Na_2SO_4.

The remainder of the amalgam was, therefore, allowed to stand for 3 hours, with frequent shaking, under 300 cc. of a saturated solution of strontium chloride, containing a little strontium hydroxide. Analysis:

61 grams of the resulting amalgam gave 2.6326 grams $SrSO_4$ and 0.0180 gram Na_2SO_4.

Of this amalgam 391 grams were diluted with 425 grams of mercury, so that the product contained 0.987 per cent of strontium and 0.005 per cent of sodium.

Strontium amalgam should be kept in a small, tightly stoppered bottle. Although only slowly acted upon by water, it is very rapidly decomposed by the air.

Calcium Amalgam.—This amalgam was prepared by the electrolysis, in a beaker, of a saturated solution of pure calcium acetate. The cathode was a kilogram of mercury;

it was connected with the negative pole of the storage circuit by means of a platinum wire, surrounded by a glass tube, into which it was fused. The anode was a horizontally disposed piece of platinum foil. Current 14 volts and 3–4 amperes. During the electrolysis the mercury was frequently stirred with a glass rod. At the end of the operation, which lasted about 30 minutes, the solution was decanted and the surface of the amalgam washed once by decantation. The amalgam was further washed by pouring it through 3 portions of about 200 cc. of water, from one beaker to another, the wash-water being decanted each time. It was, finally, dried with filter paper and bottled. This amalgam was used within 1 hour of its preparation. Analysis:

100 grams of the amalgam gave 0.0423 gram CaO.

It therefore contained 0.0302 per cent of calcium.

Calcium amalgam is more rapidly acted upon by water than either barium or strontium amalgam, and it is exceedingly unstable in the presence of air.

The analyses given above were performed immediately after the preparation of the amalgams. Most of the amalgams did not remain homogeneous; they separated into a liquid and a crystalline portion and in taking out samples no effort was made to have their composition correspond with that of the amalgams as a whole. Unless otherwise stated, the amalgams used in the following experiments were the same as those mentioned above.

With but few exceptions, the salts used in the preparation of the solutions employed were obtained from Kahlbaum. Those which were not of his manufacture were of the chemically pure variety, and came through Eimer and Amend.

METHOD OF WORK.

In the experiments to be described below, except where otherwise stated, the following was the method of procedure: The amalgam and the solution in question were brought together in a 250 cc. beaker. Four other similar beakers were taken, each containing about 100 cc. of distilled water. After the amalgam and solution had been allowed to act the re-

quired length of time, during which the beaker containing them was frequently agitated, the solution was decanted and the amalgam immediately washed once by decantation. It was then poured into beaker No. 2, containing distilled water. This beaker was quickly shaken, the wash-water decanted, and the same operation repeated until the amalgam eventually reached beaker No. 5. The water in this beaker was also decanted and the amalgam was finally decomposed in it with dilute hydrochloric acid. The acid extracts were analyzed according to methods given in Treadwell's Quantitative Analysis.

The method of washing described above is very thorough and, with practice, the entire operation can be carried out in about 1 minute. The composition of the amalgams is not seriously affected during the washing.

I. POTASSIUM AND SODIUM.

The Action of Potassium Amalgam on Sodium Chloride Solution, and of Sodium Amalgam on Potassium Chloride Solution.—Approximately equimolecular liquid potassium and sodium amalgams were prepared by the addition of 2.5 grams of potassium and 1.5 grams of sodium, respectively, to 500 grams of mercury; and solutions of the chlorides of the 2 metals were made by dissolving 29.2 grams of sodium chloride and 37.2 grams of potassium chloride, each in 100 cc. of water. The following experiments were performed:

(1) Fifty grams of potassium amalgam were treated for 15 minutes, at 28°, with 50 cc. of sodium chloride solution. Hydrogen was very slowly evolved.

The resulting amalgam gave on analysis KCl + NaCl = 0.2705 gram; K_2PtCl_6 = 0.0329 gram.

That is, it contained 0.0053 gram potassium and 0.1026 gram sodium; in atoms K : Na = 2.95 : 97.05.

(2) Fifty grams of sodium amalgam were treated for 15 minutes, at 27°, with 50 cc. of potassium chloride solution. The evolution of hydrogen was very slow.

The resulting amalgam gave, on analysis, KCl + NaCl = 0.2927 gram; K_2PtCl_6 = 0.9003 gram.

That is, it contained 0.0064 gram sodium and 0.1451 gram potassium; in atoms, Na : K = 6.95 : 93.05.

(3) *The Preparation of Potassium Amalgam from Sodium Amalgam.*—Two hundred grams of sodium amalgam were treated with 5 separate portions, of 50 cc. each, of saturated potassium hydroxide solution. Upon shaking, after the addition of the first portion, the amalgam, which at first was pasty, solidified throughout, and the temperature rose from 23° to 26°. There was no perceptible evolution of hydrogen. In order to facilitate the removal of the sodium, the mixture was heated on the water-bath and the flask containing it was frequently shaken. Upon the application of heat, the amalgam melted and hydrogen was very feebly evolved. Before the addition of each fresh portion of the solution, the amalgam was quickly washed with cold water and, until the last treatment, it solidified each time so that the flask could be inverted without loss. At the end of the last heating the amalgam was pasty when cold. The entire operation lasted 2.5 hours. Analysis:

57 grams of the amalgam gave KCl + NaCl = 1.0797 grams. This was dissolved in cold water and the solution made up to 250 cc. One-fifth of this volume gave 0.7028 gram K_2PtCl_6. The amalgam, therefore, contained 0.989 per cent of potassium and 0.004 per cent of sodium.

(4) *The Preparation of Sodium Amalgam from Potassium Amalgam.*—One hundred grams of the amalgam, whose analysis has just been given, were treated, in the cold, with 5 successive portions, of 50 cc. each, of saturated sodium hydroxide solution. On shaking, after the addition of the first portion, the temperature fell from 23° to 21°. Hydrogen was very slowly evolved, and the amalgam became more liquid. Each portion of the solution was allowed to act for 30 minutes, and during the last half hour the mixture was heated on the water-bath. Analysis:

53 grams of the amalgam gave KCl + NaCl = 0.7154 gram; K_2PtCl_6 = none.

The amalgam, therefore, contained 0.532 per cent of sodium.

The Action of Potassium, Sodium and Lithium Amalgams on a Solution Containing Equimolecular Quantities of Sodium and Potassium Chlorides.—The amalgams used in these experiments were liquid, and the first 2 were approximately equimolecular; they consisted of a solution of 2.5 grams of potassium and of 1.5 grams of sodium, each in 500 grams of mercury. The solution employed was made by dissolving a mixture of 29.2 grams of sodium chloride and 37.2 grams of potassium chloride in water and diluting the solution to 250 cc.

(5) Fifty grams of potassium amalgam were treated for 30 minutes with 50 cc. of the solution mentioned. The evolution of hydrogen was very feeble, and the temperature remained constant at 25°.

The resulting amalgam gave, on analysis, KCl + NaCl = 0.2967 gram; K_2PtCl_6 = 0.2820 gram.

That is, it contained 0.0452 gram potassium and 0.0829 gram sodium; in atoms, K: Na = 24.30: 75.70.

(6) Fifty grams of sodium amalgam were treated for 30 minutes with 50 cc. of the same solution. The evolution of hydrogen was very feeble and the temperature remained constant at 24°.5.

The resulting amalgam gave, on analysis, KCl + NaCl = 0.2616 gram; K_2PtCl_6 = 0.2352 gram.

That is, it contained 0.0377 gram potassium and 0.0746 gram sodium; in atoms, K: Na = 22.93: 77.07.

(7) Fifty grams of lithium amalgam were treated for 30 minutes, at 17°, with 50 cc. of the same solution. The evolution of hydrogen in this case was also very feeble.

The resulting amalgam gave, on analysis, KCl + NaCl = 0.0599 gram; K_2PtCl_6 = 0.0540 gram.

That is, it contained 0.0087 gram potassium and 0.0171 gram sodium; in atoms, K: Na = 23.05: 76.95.

The alcoholic filtrate from the potassium chlorplatinate was evaporated to dryness and the residue tested spectroscopically for lithium. None of that metal was present.

II. POTASSIUM AND LITHIUM.

(8) *The Action of Potassium Amalgam on Lithium Chloride Solution.*—Fifty grams of potassium amalgam were treated

for 30 minutes, at 33°, with 25 cc. of a solution containing 12.5 grams of lithium chloride. The evolution of hydrogen was more rapid than that produced by the action of the same amalgam on water.

The resulting amalgam gave, on analysis, KCl + LiCl = 0.5867 gram; K_2PtCl_6 = 0.9354 gram.

That is, it contained 0.1500 gram potassium and 0.0498 gram lithium; in atoms, K : Li = 35.11 : 64.88.

(9) *The Action of Lithium Amalgam on Potassium Chloride Solution.*—Forty grams of lithium amalgam were treated for 30 minutes with 50 cc. of a saturated solution of potassium chloride. The evolution of hydrogen was exceedingly feeble and the temperature remained constant at 19°.

The resulting amalgam gave, on analysis, KCl + LiCl = 0.1708 gram; Li_2SO_4 = none.

It, therefore, contained 0.0896 gram potassium, equivalent to 0.0161 gram lithium.

III. POTASSIUM AND BARIUM.

(10) *The Action of Potassium Amalgam on Barium Chloride Solution.*—Fifty grams of a liquid amalgam, made from 2.5 grams of potassium and 500 grams of mercury, were treated for 10 minutes with 50 cc. of a solution made by diluting saturated barium chloride solution with an equal volume of water. An exceedingly feeble evolution of hydrogen took place and the temperature rose from 22°.7 to 23°.1.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.5824 gram; K_2SO_4 = none.

It contained, therefore, 0.3427 gram barium, equivalent to 0.1953 gram potassium.

(11) *The Action of Barium Amalgam on Potassium Chloride Solution.*—Fifty grams of barium amalgam, prepared by the electrolysis of a solution of barium chloride with a mercury cathode (cf. calcium amalgam), were treated for 1 hour, at 23°, with 50 cc. of a saturated solution of potassium chloride. The evolution of hydrogen was moderately rapid.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.5710 gram; K_2SO_4 = 0.0007 gram.

That is, it contained 0.3360 gram barium and 0.0003 gram potassium; in atoms, Ba : K = 99.67 : 2(0.32).

The K_2SO_4 residue weighed 0.0012 gram and, viewed through a blue glass, it gave a good potassium flame. A blank experiment, performed at the same time, gave a residue which weighed 0.0005 gram.

(12) *The Action of Barium Amalgam on Potassium Sulphate Solution.*—Fifty grams of electrolytic barium amalgam (Exp. 11) were treated for 1 hour, at 23°, with 50 cc. of a saturated solution of potassium sulphate. The evolution of hydrogen was exceedingly feeble and the liquid became moderately turbid with barium sulphate.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.6713 gram; K_2SO_4 = 0.0103 gram.

That is, it contained 0.3950 gram barium and 0.0046 gram potassium; in atoms, Ba : K = 96.05 : 2(3.94).

The potassium sulphate residue in this case weighed 0.0108 gram. It gave a good potassium flame, and with chlorplatinic acid and alcohol a precipitate of potassium chlorplatinate.

(13) *The Action of Barium Amalgam on Potassium Carbonate Solution.*—Forty grams of barium amalgam were treated for 1 hour, at 25°, with 50 cc. of a 50 per cent potassium carbonate solution. No perceptible evolution of hydrogen took place, but the solution clouded up rapidly, owing to the formation of barium carbonate.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.0031 gram; K_2SO_4 = 0.1195 gram.

That is, it contained 0.0018 gram barium and 0.0536 gram potassium; in atoms, Ba : K = 1.88 : 2(98.12).

(14) *The Action of Barium Amalgam on Potassium Hydroxide Solution.*—Twenty-eight grams of barium amalgam were treated for 1 hour, at 23°, with 25 cc. of a saturated solution of potassium hydroxide. There was no perceptible evolution of hydrogen, but barium hydroxide separated in solid flakes. The barium hydroxide formed in the solution gave 0.2038 gram barium sulphate, equivalent to 0.0684 gram potassium.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.1589 gram; K_2PtCl_6 = 0.4104 gram.

That is, it contained 0.0935 gram barium and 0.0661 gram potassium; in atoms, Ba : K = 44.63 : 2(55.37).

IV. POTASSIUM AND STRONTIUM.

(15) *The Action of Potassium Amalgam on Strontium Chloride Solution.*—Fifty grams of potassium amalgam were treated for 15 minutes, at 21°, with a solution of 15 grams of crystallized strontium chloride in 50 cc. of water. The evolution of hydrogen was moderate.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.8141 gram; K_2SO_4 = 0.0359 gram.

That is, it contained 0.0161 gram potassium and 0.3883 gram strontium; in atoms, K : Sr = 4.43 : ½(95.57).

(16) *The Action of Strontium Amalgam on Potassium Chloride Solution.*—Forty grams of strontium amalgam were treated, for 30 minutes, at 23°, with 50 cc. of a saturated solution of potassium chloride. A very feeble evolution of hydrogen took place.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.2960 gram; K_2SO_4 = 0.1105 gram.

That is, it contained 0.1412 gram strontium and 0.0496 gram potassium; in atoms, Sr : K = 71.81 : 2(28.21).

(17) *The Action of Strontium Amalgam on Potassium Sulphate Solution.*—Forty grams of strontium amalgam were treated, for 1 hour, at 25°, with 50 cc. of a saturated solution of potassium sulphate. There was practically no evolution of hydrogen, but the solution rapidly clouded up, owing to the formation of strontium sulphate.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.6116 gram; K_2SO_4 = 0.1053 gram.

That is, it contained 0.2917 gram strontium and 0.0473 gram potassium; in atoms, Sr : K = 84.65 : 2(15.35).

(18) *The Action of Strontium Amalgam on Potassim Carbonate Solution.*—Forty grams of strontium amalgam were treated for 1 hour with 50 cc. of a 50 per cent potassium carbonate solution. There was a very feeble evolution of hydrogen, the solution rapidly became cloudy, owing to the forma-

tion of strontium carbonate, and the temperature rose slowly from 22° to 24°.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.0977 gram; K_2SO_4 = 0.5919 gram.

That is, it contained 0.0466 gram strontium and 0.2658 gram potassium; in atoms, Sr: K = 13.55: 2(86.45).

(19) *The Action of Strontium Amalgam on Potassium Hydroxide Solution.*—Fifty grams of strontium amalgam were treated for 15 minutes with 50 cc. of saturated potassium hydroxide solution. The evolution of hydrogen was imperceptible and the temperature rose from 25° to 27°. Solid strontium hydroxide separated in quantity.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.5131 gram; K_2SO_4 = 0.5774 gram.

That is, it contained 0.2447 gram strontium and 0.2593 gram potassium; in atoms, Sr: K = 45.75: 2(54.25).

V. POTASSIUM AND CALCIUM.

(20) *The Action of Potassium Amalgam on Calcium Chloride Solution.*—Fifty grams of potassium amalgam were treated for 15 minutes, at the ordinary temperature, with 20 cc. of a 50 per cent calcium chloride solution. The evolution of hydrogen was much more rapid than that which the same amalgam gave with water; the surface of the amalgam became covered in spots with a dark deposit, and later the solution became gray and turbid, owing to the presence of very finely divided mercury.

The resulting amalgam gave, on analysis, CaO = 0.0830 gram; K_2SO_4 = 0.7758 gram.

That is, it contained 0.3484 gram potassium and 0.0593 gram calcium; in atoms, K: Ca = 75.01: ½(24.99).

(21) *The Action of Calcium Amalgam on Potassium Chloride Solution.*—One hundred grams of calcium amalgam were treated for 30 minutes, at 20°, with 50 cc. of a saturated solution of potassium chloride. The evolution of hydrogen was very feeble.

The resulting amalgam gave, on analysis, CaO = 0.0230 gram; K_2SO_4 = 0.0348 gram.

That is, it contained 0.0164 gram calcium and 0.0156 gram potassium; in atoms, Ca : K = 50.66 : 2(49.33).

(22) *The Action of Calcium Amalgam on Potassium Hydroxide Solution.*—Fifty grams of calcium amalgam were treated for 30 minutes, at the ordinary temperature, with 50 cc. of a saturated solution of potassium hydroxide. There was no perceptible evolution of hydrogen, but calcium hydroxide separated in solid form at the surface of the amalgam. The potassium hydroxide mother liquor gave 0.0254 gram calcium oxide, equivalent to 0.0354 gram potassium.

The resulting amalgam gave, on analysis, CaO = 0.0110 gram; K_2SO_4 = 0.0728 gram.

That is, it contained 0.0078 gram calcium and 0.0327 gram potassium; in atoms, Ca : K = 31.78 : 2(68.22).

VI. POTASSIUM AND MAGNESIUM.

(23) *The Action of Potassium Amalgam on Magnesium Sulphate Solution.*—Fifty grams of potassium amalgam were treated for 10 minutes, at 24°, with 25 cc. of a saturated solution of magnesium sulphate. The evolution of hydrogen was more rapid than that which the same amalgam gave with water.

The resulting amalgam gave, on analysis, $K_2SO_4 + MgSO_4$ = 0.8730 gram; $Mg_2P_2O_7$ = 0.0089 gram.

That is, it contained 0.3878 gram potassium and 0.0019 gram magnesium; in atoms, K : Mg = 98.45 : ½(1.55).

(24) *The Action of Magnesium Amalgam on Potassium Hydroxide Solution.*—To 200 grams of mercury in a 250 cc. beaker, 1 gram of bright magnesium ribbon was added, in short pieces. In order to bring about amalgamation, the metals were just covered with water and a little very dilute hydrochloric acid was added. Then, after having stirred the mixture, a solution of 70 grams of potassium hydroxide in 50 cc. of water was added. The temperature was 35°. The strips of magnesium were pressed down on the mercury with a glass rod from time to time during the action, which was allowed to continue for 1 hour. There was a moderate evolution of hydrogen, especially from the pieces of magnesium which were

in contact with the mercury, and these were considerably corroded, though bright, at the end of the action. In washing the amalgam, the liquid metal was readily poured away from the strips of magnesium.

The resulting amalgam gave, on analysis, $MgSO_4 + K_2SO_4$ = 0.4407 gram; $MgNH_4PO_4$ = none.

It, therefore, contained 0.1979 gram potassium, equivalent to 0.0616 gram magnesium.

VII. SODIUM AND LITHIUM.

(25) *The Action of Sodium Amalgam on Lithium Chloride Solution.*—Fifty grams of sodium amalgam were treated for 30 minutes, at 35°, with 25 cc. of a solution containing 12.5 grams of lithium chloride. The evolution of hydrogen, which was slow at first, became more and more rapid, until it approached in rapidity that produced by the action of potassium amalgam on the same solution (Exp. 8).

The resulting amalgam gave, on analysis, NaCl + LiCl = 1.1570 grams; Li_2SO_4 = 0.0352 gram.

That is, it contained 0.4451 gram sodium and 0.0045 gram lithium; in atoms, Na : Li = 96.79 : 3.21.

(26) *The Action of Lithium Amalgam on Sodium Chloride Solution.*—Forty grams of lithium amalgam were treated for 30 minutes, at 18°, with 50 cc. of a saturated solution of sodium chloride. The evolution of hydrogen was exceedingly feeble.

The resulting amalgam gave, on analysis, NaCl + LiCl = 0.0948 gram; Li_2SO_4 = none.

It, therefore, contained 0.0373 gram sodium, equivalent to 0.0114 gram lithium.

VIII. SODIUM AND BARIUM.

(27) *The Action of Sodium Amalgam on Barium Chloride Solution.*—Fifty grams of a liquid amalgam, made by the addition of 1.5 grams of sodium to 500 grams of mercury, were treated, for 10 minutes, with 50 cc. of a solution made by diluting saturated barium chloride solution with an equal volume of water. An exceedingly feeble evolution of hydrogen took place and the temperature rose from 22°.5 to 23°.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.5293 gram; Na_2SO_4 = none.

It, therefore, contained 0.3114 gram barium, equivalent to 0.1304 gram sodium.

(28) *The Action of Barium Amalgam on Sodium Chloride Solution.*—Fifty grams of electrolytic barium amalgam (Exp. 11) were treated for 1 hour, at 23°, with 50 cc. of a saturated solution of sodium chloride. The evolution of hydrogen was very slow.

The resulting amalgam gave, on analysis, $BaSO_4$ = 1.0499 grams; Na_2SO_4 = 0.0021 gram.

That is, it contained 0.6178 gram barium and 0.0007 gram sodium; in atoms, Ba: Na = 99.35: 2(0.65).

(29) *The Action of Barium Amalgam on Sodium Sulphate Solution.*—Fifty grams of electrolyic barium amalgam (Exp. 11) were treated for 1 hour, at 23°, with 50 cc. of a saturated solution of sodium sulphate. The evolution of hydrogen was very feeble, but faster than that which the same amalgam gave with potassium sulphate solution (Exp. 12). Also more barium sulphate was formed in the aqueous liquid.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.6838 gram; Na_2SO_4 = 0.0029 gram.

That is, it contained 0.4024 gram barium and 0.0009 gram sodium; in atoms, Ba: Na = 98.63: 2(1.37)

(30) *The Action of Barium Amalgam on Sodium Carbonate Solution.*—Forty grams of barium amalgam were treated for 1 hour, at 24°, with 50 cc. of a solution of 20 grams of anhydrous sodium carbonate in 100 cc. of water. There was no perceptible evolution of hydrogen, but the solution became clouded with barium carbonate.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.1183 gram; Na_2SO_4 = 0.0290 gram.

That is, it contained 0.0696 gram barium and 0.0094 gram sodium; in atoms, Ba: Na = 71.29: 2(28.71).

(31) *The Action of Barium Amalgam on Sodium Hydroxide Solution.*—Sixty grams of barium amalgam were treated for 65 minutes, at 45°, with 100 cc. of a saturated solution of sodium

hydroxide. There was no perceptible evolution of hydrogen, but barium hydroxide separated in quantity.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.0415 gram; Na_2SO_4 = 0.1868 gram.

That is, it contained 0.0244 gram barium and 0.0606 gram sodium; in atoms, Ba : Na = 11.91 : 2(88.09).

IX. SODIUM AND STRONTIUM.

(32) *The Action of Sodium Amalgam on Strontium Chloride Solution.*—Fifty grams of sodium amalgam were treated for 25 minutes, at 18°, with a solution of 15 grams of crystalline strontium chloride in 50 cc. of water. A moderately rapid evolution of hydrogen took place.

The resulting amalgam gave, on analysis, $SrSO_4$ = 1.6891 grams; $NaSO_4$ = 0.5906 gram.

That is, it contained 0.1915 gram sodium and 0.8057 gram strontium; in atoms, Na : Sr = 31.11 : ½(68.89).

(33) *The Action of Strontium Amalgam on Sodium Chloride Solution.*—Forty grams of strontium amalgam were treated for 30 minutes, at 25°, with 50 cc. of a saturated sodium chloride solution. The evolution of hydrogen was moderate.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.2337 gram; Na_2SO_4 = 0.0755 gram.

That is, it contained 0.1115 gram strontium and 0.0245 gram sodium; in atoms, Sr : Na = 70.55 : 2(29.45).

(34) *The Action of Strontium Amalgam on Sodium Sulphate Solution.*—Forty grams of strontium amalgam were treated, for 1 hour, with 50 cc. of a saturated solution of sodium sulphate. The evolution of hydrogen was practically imperceptible, the temperature remained constant at 26°, and the solution rapidly clouded up, owing to the formation of strontium sulphate.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.0693 gram; Na_2SO_4 = 0.4541 gram.

That is, it contained 0.0331 gram strontium and 0.1473 gram sodium; in atoms, Sr : Na = 10.57 : 2(89.43).

(35) *The Action of Strontium Amalgam on Sodium Carbonate Solution.*—Forty grams of strontium amalgam were

treated for 1 hour, at 22°, with 50 cc. of a solution of 20 grams of anhydrous sodium carbonate in 100 cc. of water. The evolution of hydrogen was very feeble and the solution became turbid, owing to the formation of strontium carbonate.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.4201 gram; Na_2SO_4 = 0.1998 gram.

That is, it contained 0.2004 gram strontium and 0.0648 gram sodium; in atoms, Sr : Na = 61.94 : 2(38.06).

(36) *The Action of Strontium Amalgam on Sodium Hydroxide Solution.*—Fifty grams of strontium amalgam were treated, for 15 minutes, with 50 cc. of a saturated solution of sodium hydroxide. There was no perceptible evolution of hydrogen. The temperature rose from 25° to 26°.5, and solid flakes of strontium hydroxide separated at the surface of the amalgam.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.2092 gram; Na_2SO_4 = 0.6263 gram.

That is, it contained 0.0998 gram strontium and 0.2031 gram soidum; in atoms, Sr : Na = 20.54 : 2(79.46).

X. SODIUM AND CALCIUM.

(37) *The Action of Sodium Amalgam on Calcium Chloride Solution.*—Fifty grams of sodium amalgam were treated, for 15 minutes, at the ordinary temperature, with 20 cc. of a 50 per cent solution of calcium chloride. A moderately rapid evolution of hydrogen took place, but the solution did not become turbid with finely divided mercury as it did when acted upon by potassium amalgam (Exp. 20).

The resulting amalgam gave, on analysis, CaO = 0.0216 gram; Na_2SO_4 = 1.6117 grams.

That is, it contained 0.5226 gram sodium and 0.0154 gram calcium; in atoms, Na : Ca = 96.72 : ½(3.28).

(38) *The Action of Calcium Amalgam on Sodium Chloride Solution.*—One hundred grams of calcium amalgam were treated for 30 minutes, at 20°, with 50 cc. of a saturated solution of sodium chloride. The evolution of hydrogen was very feeble.

The resulting amalgam gave, on analysis, CaO = 0.0157 gram; Na_2SO_4 = 0.0569 gram.

That is, it contained 0.0112 gram calcium and 0.0184 gram sodium; in atoms, Ca: Na = 25.90: 2(74.09).

(39) *The Action of Calcium Amalgam on Sodium Hydroxide Solution.*—Sixty grams of calcium amalgam were treated for 30 minutes, at the ordinary temperature, with 50 cc. of a saturated solution of sodium hydroxide. There was no perceptible evolution of hydrogen, but calcium hydroxide separated in solid form. The sodium hydroxide mother liquor contained 0.0342 gram calcium oxide, equivalent to 0.0280 gram sodium.

The resulting amalgam gave, on analysis, CaO = 0.0015 gram; Na_2SO_4 = 0.0787 gram.

This is equivalent to 0.0011 gram calcium and 0.0255 gram sodium; in atoms, Ca: Na = 4.72: 2(95.27).

XI. SODIUM AND MAGNESIUM.

(40) *The Action of Sodium Amalgam on Magnesium Sulphate Solution.*—Fifty grams of sodium amalgam were treated for 10 minutes, at 24°, with 25 cc. of a saturated solution of magnesium sulphate. The evolution of hydrogen was more rapid than that which the same amalgam gave with water.

The resulting amalgam gave, on analysis, $Na_2SO_4 + MgSO_4$ = 1.6396 grams; $Mg_2P_2O_7$ = 0.0069 gram.

That is, it contained 0.5293 gram sodium and 0.0015 gram magnesium; in atoms, Na: Mg = 99.47: ½(0.53).

(41) *The Action of Magnesium Amalgam on Sodium Hydroxide Solution.*—To 200 grams of mercury, in a 250 cc. beaker, 1 gram of bright magnesium ribbon was added, in short strips. The metals were then just covered with water and a little very dilute hydrochloric acid was added. After having stirred the mixture, a solution of 50 grams of sodium hydroxide, in 50 cc. of water, was added. The temperature was 39°. During the action, which was allowed to continue for 1 hour, the strips of magnesium were pressed down on the mercury from time to time with a glass rod. The evolution of hydrogen was much slower in this case than it was under the same conditions with potassium hydroxide solution (Exp. 24), and the strips of magnesium were also much less corroded at the end

of the action. In washing, the liquid amalgam was readily poured off from the strips of magnesium.

The resulting amalgam gave, on analysis, $MgSO_4 + Na_2SO_4$ = 0.1235 gram; $MgNH_4PO_4$ = none.

It, therefore, contained, 0.4000 gram sodium, equivalent to 0.0211 gram magnesium.

XII. LITHIUM AND BARIUM.

(42) *The Action of Lithium Amalgam on Barium Chloride Solution.*—Forty grams of lithium amalgam were treated for 10 minutes, at 26°, with 50 cc. of saturated barium chloride solution. The evolution of hydrogen was exceedingly feeble.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.2920 gram; Li_2SO_4 = none.

It, therefore, contained 0.1718 gram barium, equivalent to 0.0176 gram lithium.

(43) *The Action of Barium Amalgam on Lithium Chloride Solution.*—Fifty grams of barium amalgam were treated for 30 minutes, at 30°, with 25 cc. of a solution containing 12.5 grams of lithium chloride. The evolution of hydrogen was very slow.

The amalgam gave, on analysis, $BaSO_4$ = 0.1491 gram; Li_2SO_4 = none.

(44) *The Action of Barium Amalgam on Lithium Sulphate Solution.*—Fifty grams of barium amalgam were treated for 30 minutes, at 25°, with 25 cc. of a solution containing 6 grams of crystalline lithium sulphate. The evolution of hydrogen was very slow and very little barium sulphate was formed.

The amalgam gave, on analysis, $BaSO_4$ = 0.1777 gram; Li_2SO_4 = none.

(45) *The Action of Barium Amalgam on Lithium Hydroxide Solution.*—Fifty grams of barium amalgam were treated for 30 minutes, at 24°, with 50 cc. of saturated lithium hydroxide solution. The evolution of hydrogen was barely perceptible.

The amalgam gave, on analysis, $BaSO_4$ = 0.1454 gram; Li_2SO_4 = none.

(46) *The Action of Barium Amalgam on a Mixed Lithium Chloride, Hydroxide and Sulphate Solution.*—Fifty grams of

electrolytic barium amalgam (Exp. 11) were treated for 1 hour, at 23°, with 50 cc. of a solution made by dissolving 15 grams of lithium chloride and 2 grams of crystalline lithium sulphate in a mixture of 25 cc. of saturated lithium hydroxide solution and 75 cc. of water. An exceedingly feeble evolution of hydrogen took place and the solution became slightly turbid.

The amalgam gave, on analysis, $BaSO_4$ = 0.7079 gram; Li_2SO_4 = none.

XIII. LITHIUM AND STRONTIUM.

(47) *The Action of Lithium Amalgam on Strontium Chloride Solution.*—Forty grams of lithium amalgam were treated for 15 minutes, at 26°, with a solution of 15 grams of crystalline strontium chloride in 50 cc. of water. A very feeble evolution of hydrogen took place.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.2155 gram; Li_2SO_4 = none.

It, therefore, contained 0.1028 gram strontium, equivalent to 0.0165 gram lithium.

(48) *The Action of Strontium Amalgam on Lithium Chloride Solution.*—Fifty grams of strontium amalgam, made by the electrolysis of a solution of strontium chloride with a mercury cathode, were treated for 1 hour, at 23°, with 50 cc. of a solution containing 25 grams of lithium chloride. The evolution of hydrogen was moderately rapid.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.2545 gram; Li_2SO_4 = 0.0013 gram.

That is, it contained 0.1214 gram strontium and 0.00016 gram lithium; in atoms, Sr: Li = 98.32: 2(1.67).

The lithium sulphate residue gave the spectroscopic test for lithium.

(49) *The Action of Strontium Amalgam on Lithium Sulphate Solution.*—Fifty grams of electrolytic strontium amalgam (Exp. 48) were treated for 1 hour, at 23°, with a solution of 10 grams of crystalline lithium sulphate, in 40 cc. of water. The evolution of hydrogen was moderately rapid and strontium sulphate was formed in large quantity.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.4988 gram; Li_2SO_4 = 0.0037 gram.

That is, it contained 0.2379 gram strontium and 0.00047 gram lithium; in atoms, Sr: Li = 97.58: 2(2.41).

The lithium sulphate residue gave a very bright and persistent lithium spectrum.

(50) *The Action of Strontium Amalgam on Lithium Hydroxide Solution.*—Fifty grams of electrolytic strontium amalgam (Exp. 48) were treated for 1 hour, at 22°, with 25 cc. of a saturated solution of lithium hydroxide. The evolution of hydrogen was very feeble.

The resulting amalgam gave, on analysis, $SrSO_4$ = 1.2509 grams; Li_2SO_4 = 0.0087 gram.

That is, it contained 0.5980 gram strontium and 0.0011 gram lithium; in atoms, Sr: Li = 97.74: 2(2.26).

The lithium sulphate residue gave an especially bright and persistent lithium spectrum.

XIV. LITHIUM AND CALCIUM.

(51) *The Action of Lithium Amalgam on Calcium Chloride Solution.*—Thirty-five grams of lithium amalgam were treated for 15 minutes, at 24°, with 50 cc. of a 50 per cent calcium chloride solution. The evolution of hydrogen was rapid at first, but it gradually slowed down.

The resulting amalgam gave, on analysis, CaO = 0.0270 gram; Li_2SO_4 = none.

It, therefore, contained 0.0193 gram calcium, equivalent to 0.0067 gram lithium.

(52) *The Action of Calcium Amalgam on Lithium Chloride Solution.*—One hundred grams of calcium amalgam were treated for 30 minutes, at 20°, with 50 cc. of a solution containing 37.5 grams of lithium chloride. The evolution of hydrogen was slow.

The resulting amalgam gave, on analysis, CaO = 0.0320 gram; Li_2SO_4 = 0.0033 gram.

That is, it contained 0.0229 gram calcium and 0.00042 gram lithium; in atoms, Ca: Li = 90.49: 2(9.50).

The lithium sulphate residue gave a good lithium spectrum.

(53) *The Action of Calcium Amalgam on Lithium Hydroxide Solution.*—One hundred grams of calcium amalgam were treated for 30 minutes, at 20°, with 50 cc. of a saturated solution of lithium hydroxide. The evolution of hydrogen was very slow.

The resulting amalgam gave, on analysis, CaO = 0.0290 gram; Li_2SO_4 = 0.0114 gram.

That is, it contained 0.0207 gram calcium and 0.0014 gram lithium; in atoms, Ca: Li = 71.40: 2(28.60).

The lithium sulphate residue gave a bright and very persistent lithium spectrum.

XV. LITHIUM AND MAGNESIUM.

(54) *The Action of Lithium Amalgam on Magnesium Sulphate Solution.*—Forty grams of lithium amalgam were treated for 10 minutes, at 22°, with 25 cc. of a saturated solution of magnesium sulphate. The evolution of hydrogen was at first very rapid, but it quickly slowed down.

On analysis, the mercury was found to contain neither lithium nor magnesium.

(55) *The Action of Magnesium Amalgam on a Mixed Lithium Chloride and Hydroxide Solution.*—To 200 grams of mercury, in a 250 cc. beaker, 0.5 gram of bright magnesium ribbon was added, in short strips. The surface of the metals was just covered with water and then 1 cc. of 3 per cent hydrochloric acid was added. After having stirred the mixture, a solution of 15 grams of lithium chloride, in a mixture of 10 cc. of saturated lithium hydroxide solution and 25 cc. of water, was added. The temperature was 24°. The evolution of hydrogen was rapid and a very dark deposit of finely divided mercury was formed which soon rendered the solution dark and opaque. The action was allowed to continue for 1 hour.

The resulting amalgam gave, on analysis, Li_2SO_4 = 0.0486 gram.

It, therefore, contained 0.0062 gram lithium, equivalent to 0.0105 gram magnesium.

XVI. BARIUM AND STRONTIUM.

(56) *The Action of Barium Amalgam on Strontium Chloride Solution.*—Fifty grams of electrolytic barium amalgam (Exp. 11) were treated for 1 hour, at 22°, with 50 cc. of a saturated solution of strontium chloride. The evolution of hydrogen was very feeble.

The amalgam gave, on analysis, $BaCrO_4$ = 0.5292 gram; $SrSO_4$ = none.

(57) *The Action of Strontium Amalgam on Barium Chloride Solution.*—Fifty grams of strontium amalgam were treated for 10 minutes, at 26°, with 50 cc. of a saturated solution of barium chloride. The evolution of hydrogen was slow.

The resulting amalgam gave, on analysis, $BaCrO_4$ = 0.9476 gram; $SrSO_4$ = 0.2466 gram.

That is, it contained 0.1176 gram strontium and 0.5136 gram barium; in atoms, Sr: Ba = 26.43: 73.57.

XVII. BARIUM AND CALCIUM.

(58) *The Action of Barium Amalgam on Calcium Chloride Solution.*—Fifty grams of electrolytic barium amalgam (Exp. 11) were treated for 1 hour, at 19°, with 50 cc. of a saturated solution of calcium chloride. The evolution of hydrogen was at first very slow, but it gradually became more rapid; during the last 45 minutes it was moderate.

The resulting amalgam gave, on analysis, $BaCrO_4$ = 0.3820 gram; CaC_2O_4 = none.

(59) *The Action of Calcium Amalgam on Barium Chloride Solution.*—One hnndred grams of calcium amalgam were treated for 30 minutes, at 20°, with 50 cc. of a saturated solution of barium chloride. The evolution of hydrogen was exceedingly slow.

The resulting amalgam gave, on analysis, CaO = 0.0219 gram; $BaSO_4$ = 0.0663 gram.

That is, it contained 0.0156 gram calcium and 0.0390 gram barium; in atoms, Ca: Ba = 57.89: 42.11.

XVIII. BARIUM AND MAGNESIUM.

(60) *The Action of Barium Amalgam on Magnesium Sulphate Solution.*—Fifty grams of electrolytic barium amalgam

(Exp. 11) were treated for 1 hour, at 22°, with 50 cc. of a saturated solution of magnesium sulphate. The evolution of hydrogen was moderately rapid and about 0.1 gram of barium sulphate was formed in the solution.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.3476 gram; $Mg_2P_2O_7$ = 0.0022 gram.

It, therefore, contained 0.2045 gram barium and 0.00048 gram magnesium; in atoms, Ba : Mg = 98.69 : 1.31.

(61) *The Action of Magnesium Amalgam on Barium Chloride Solution.*—The surface of 200 grams of mercury, in a 150 cc. beaker, was just covered with water, and under this was introduced 0.2 gram of brightly polished magnesium ribbon, in short pieces. To the mixture 1 cc. of 3 per cent hydrochloric acid was added, and then, after a few seconds, 50 cc. of saturated barium chloride solution. After 20 minutes the solution was neutral to litmus and the evolution of hydrogen was still moderate. The temperature was 24°. The action was allowed to continue for 1 hour.

The resulting amalgam gave, on analysis, $BaSO_4$ = 0.2665 gram; $MgNH_4PO_4$ = none.

It, therefore, contained 0.1568 gram barium, equivalent to 0.0278 gram magnesium.

XIX. STRONTIUM AND CALCIUM.

(62) *The Action of Strontium Amalgam on Calcium Chloride Solution.*—Fifty grams of electrolytic strontium amalgam (Exp. 48) were treated for 15 minutes, at 20°, with 50 cc. of a saturated solution of calcium chloride. The evolution of hydrogen was rapid.

The resulting amalgam gave, on analysis, CaO = 0.0108 gram; $SrSO_4$ = 1.1160 grams.

That is, it contained 0.5323 gram strontium and 0.0077 gram calcium; in atoms, Sr : Ca = 96.93 : 3.07.

(63) *The Action of Calcium Amalgam on Strontium Chloride Solution.*—One hundred grams of calcium amalgam were treated for 30 minutes, at 20°, with 50 cc. of a saturated solution of strontium chloride. The evolution of hydrogen was

very slow; it was much faster, however, than that which the same amalgam gave with barium chloride solution (Exp. 59).

The resulting amalgam gave, on analysis, CaO = 0.0109 gram; $SrSO_4$ = 0.0892 gram.

That is, it contained 0.0078 gram calcium and 0.0425 gram strontium; in atoms, Ca : Sr = 28.57 : 71.42.

XX. STRONTIUM AND MAGNESIUM.

(64) *The Action of Strontium Amalgam on Magnesium Sulphate Solution.*—Fifty grams of electrolytic strontium amalgam (Exp. 48) were treated for 30 minutes, at 22°, with 50 cc. of a saturated solution of magnesium sulphate. The evolution of hydrogen was much faster than that given by the same solution with barium amalgam, and about 0.3 gram of strontium sulphate was formed in the solution (cf. Exp. 60).

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.9679 gram; $Mg_2P_2O_7$ = 0.0031 gram.

That is, it contained 0.4616 gram strontium and 0.00068 gram magnesium; in atoms, Sr : Mg = 99.48 : 0.52.

(65) *The Action of Magnesium Amalgam on Strontium Chloride Solution.*—The surface of 200 grams of mercury, in a 150 cc. beaker, was just covered with water, and under this was introduced 0.2 gram of brightly polished magnesium ribbon, in short pieces. To the mixture 1 cc. of 3 per cent hydrochloric acid was added, and then, after a few seconds, 50 cc. of saturated strontium chloride solution. After 20 minutes the solution was neutral to litmus and the evolution of hydrogen was rapid. A dark deposit of finely divided mercury was formed, and this soon rendered the solution dark and turbid. The temperature was 23°. The action was allowed to continue for 1 hour.

The resulting amalgam gave, on analysis, $SrSO_4$ = 0.0068 gram; $MgNH_4PO_4$ = none.

It, therefore, contained 0.0032 gram strontium, equivalent to 0.0009 gram magnesium.

XXI. CALCIUM AND MAGNESIUM.

(66) *The Action of Calcium Amalgam on Magnesium Sulphate Solution.*—One hundred grams of calcium amalgam

were treated for 30 minutes, at 20°, with 50 cc. of a saturated solution of magnesium sulphate. The evolution of hydrogen was moderate and calcium sulphate was formed in the solution.

The resulting amalgam gave, on analysis, CaO = 0.0084 gram; $MgNH_4PO_4$ = none.

(67) *The Action of Magnesium Amalgam on Calcium Chloride Solution.*—Two hundred grams of mercury and 0.5 gram of bright magnesium ribbon were treated, as described in Experiments 61 and 65, with 50 cc. of a saturated solution of calcium chloride. After 30 minutes the solution was neutral to litmus. The temperature was 25° and the evolution of hydrogen was rapid. A very dark deposit of finely divided mercury, which soon rendered the solution opaque, was formed. The action was allowed to continue for 1 hour.

On analysis, neither calcium nor magnesium was found in the mercury.

TABULATION OF RESULTS.

In comparing the following results, allowance should be made for the differences in concentration of the various solutions employed. For example, the relative difference in the action of barium, or strontium amalgam on potassium and sodium carbonate solutions on the one hand, and on their hydroxide solutions on the other, can readily be accounted for on taking into consideration the relative concentrations of the carbonate solutions of these metals, and of their hydroxide solutions, respectively:

The atomic ratios in Experiments 49 and 50 are misleading. The amalgam used in the latter was much richer in strontium than that used in the former. More lithium, by weight, was displaced from the hydroxide solution than from either of the others. The same is true in Experiments 13 and 18; the barium amalgam used in Experiment 13 was liquid, and very dilute, while the strontium amalgam used in Experiment 18 was a mixture of liquid and solid amalgam and contained more than 1.5 per cent of strontium.

Amalgam.	Expt. No.	Solution.	Time.	Temperature.	Evolution of hydrogen.	Atomic proportions of the amalgamated metals.
Potassium	1	NaCl	15 min.	28°	very slow	K : Na = 2.95 : 97.05
	3	NaOH	2½ hours	water-bath	very feeble	0.99 per cent K
	5	KCl + NaCl	30 min.	25°	very feeble	K : Na = 24.30 : 75.70
	8	LiCl	30 min.	33°	moderate	K : Li = 35.11 : 64.88
	10	$BaCl_2$	10 min.	23°	very feeble	0.68 per cent Ba
	15	$SrCl_2$	15 min.	21°	moderate	K : Sr = 4.43 : ½(95.57)
	20	$CaCl_2$	15 min	room temp.	rapid	K : Ca = 75.01 : ½(24.99)
	23	$MgSO_4$	10 min.	24°	rapid	K : Mg = 98.45 : ½(1.55)
Sodium	2	KCl	15 min.	27°	very slow	Na : K = 6.95 : 93.05
	4	KOH	2½ hours	water-bath	very feeble	0.53 per cent Na
	6	KCl + NaCl	30 min.	24°.5	very feeble	K : Na = 22.93 : 77.07
	25	LiCl	30 min.	35°	moderate	Na : Li = 96.79 : 3.21
	27	$BaCl_2$	10 min.	23°	very feeble	0.62 per cent Ba
	32	$SrCl_2$	25 min.	18°	fairly rapid	Na : Sr = 31.11 : ½(68.89)
	37	$CaCl_2$	15 min.	room. temp.	fairly rapid	Na : Ca = 96.72 : ½(3.28)
	40	$MgSO_4$	10 min.	24°	fairly rapid	Na : Mg = 99.47 : ½(0.53)
Lithium	7	KCl + NaCl	30 min	17°	very feeble	K : Na = 23.05 : 76 : 95
	9	KCl	30 min	19°	very feeble	0.22 per cent K
	26	NaCl	30 min.	18°	very feeble	0.09 per cent Na
	42	$BaCl_2$	10 min.	26°	very feeble	0.43 per cent Ba
	47	$SrCl_2$	15 min.	26°	very feeble	0.25 per cent Sr
	51	$CaCl_2$	15 min.	24°	rapid	0.05 per cent Ca
	54	$MgSO_4$	10 min.	22°	very rapid	Pure mercury

Amalgam.	Expt. No.	Solution.	Time.	Temperature.	Evolution of hydrogen.	Atomic proportions of the amalgamated metals.
Barium	11	KCl	1 hour	23°	moderate	Ba : K = 99.67 : 2(0.32)
	12	K_2SO_4	1 hour	23°	very feeble	= 96.05 : 2(3.94)
	13	K_2CO_3	1 hour	25°	imperceptible	= 1.88 : 2(98.12)
	14	KOH	1 hour	23°	imperceptible	= 44.63 : 2(55.37)
	28	NaCl	1 hour	23°	very slow	Ba : Na = 99.35 : 2(0.65)
	29	Na_2SO_4	1 hour	23°	very slow	= 98.63 : 2(1.37)
	30	Na_2CO_3	1 hour	24°	imperceptible	= 71.29 : 2(28.71)
	31	NaOH	65 min.	45°	imperceptible	= 11.91 : 2(88.09)
	43	LiCl	30 min.	33°	very slow	0.17 per cent Ba
	44	Li_2SO_4	30 min.	25°	very slow	0.21 per cent Ba
	45	LiOH	30 min.	24°	very feeble	0.17 per cent Ba
	46	$Li(Cl,OH,\frac{1}{2}SO_4)$	1 hour	23°	very feeble	0.83 per cent Ba
	56	$SrCl_2$	1 hour	22°	very feeble	0.57 per cent Ba
	58	$CaCl_2$	1 hour	19°	moderate	0.41 per cent Ba
	60	$MgSO_4$	1 hour	22°	fairly rapid	Ba : Mg = 98.69 : 1.31
Strontium	16	KCl	30 min.	23°	very feeble	Sr : K = 71.81 : 2(28.21)
	17	K_2SO_4	1 hour	25°	imperceptible	= 84.65 : 2(15.35)
	18	K_2CO_3	1 hour	23°	very feeble	= 13.55 : 2(86.45)
	19	KOH	15 min.	26°	imperceptible	= 45.75 : 2(54.25)
	33	NaCl	30 min.	25°	moderate	Sr : Na = 70.55 : 2(29.45)
	34	Na_2SO_4	1 hour	26°	imperceptible	= 10.57 : 2(89.43)
	35	Na_2CO_3	1 hour	22°	very feeble	= 61.94 : 2(38.06)

Amalgam.	Expt. No.	Solution.	Time.	Temperature.	Evolution of hydrogen.	Atomic proportions of the amalgamated metals.
Strontium	36	NaOH	15 min.	26°	imperceptible	Sr:Na = 20.54:2(79.46)
	48	LiCl	1 hour	23°	fairly rapid	Sr:Li = 98.32:2(1.67)
	49	Li_2SO_4	1 hour	23°	fairly rapid	= 97.58:2(2.41)
	50	LiOH	1 hour	22°	very feeble	= 97.74:2(2.26)
	57	$BaCl_2$	10 min.	26°	slow	Sr:Ba = 26.43:73.57
	62	$CaCl_2$	15 min.	20°	rapid	Sr:Ca = 96.93:3.07
	64	$MgSO_4$	30 min.	22°	rapid	Sr:Mg = 99.48:0.52
Calcium	21	KCl	30 min.	20°	very feeble	Ca:K = 50.66:2(49.33).
	22	KOH	30 min.	room temp.	imperceptible	= 31.78:2(68.22)
	38	NaCl	30 min.	20°	very feeble	Ca:Na = 25.90:2(74.09)
	39	NaOH	30 min.	room temp.	imperceptible	= 4.72:2(95.27)
	52	LiCl	30 min.	20°	slow	Ca:Li = 90.49:2(9.50)
	53	LiOH	30 min.	20°	very slow	= 71.40:2(28.60)
	59	$BaCl_2$	30 min.	20°	very feeble	Ca:Ba = 57.89:42.11
	63	$SrCl_2$	30 min.	20°	very feeble	Ca:Sr = 28.57:71.42
	66	$MgSO_4$	30 min.	20°	moderate	0.006 per cent Ca
Magnesium	24	KOH	1 hour	35°	moderate	0.10 per cent K
	41	NaOH	1 hour	39°	slow	0.02 per cent Na
	55	Li(Cl,OH)	1 hour	31°	rapid	0.003 per cent Li
	61	$BaCl_2$	1 hour	24°	moderate	0.08 per cent Ba
	65	$SrCl_2$	1 hour	23°	rapid	0.0016 per cent Sr
	67	$CaCl_2$	1 hour	25°	rapid	Pure mercury

DISCUSSION OF RESULTS.

The electromotive series, in so far as concerns the metals under discussion, reads:

+K, Na, Li, Ba, Sr, Ca, Mg—.

Disregarding the action of water, we should expect each metal in this series, beginning at the positive end, to be capable of displacing from aqueous salt solutions any of the metals which follow it in the series, and, under like conditions, this displacement should take place the more readily, the farther apart the 2 metals stand in the series. In other words, applying our introductory considerations, and disregarding for the time being the action of water, we should expect, under like conditions, to have the relation,

$$\sqrt[+]{\frac{P_+}{p_+}} > \sqrt[n-]{\frac{P_-}{p_-}},$$

and the more electropositive metal should displace the more electronegative one from its salt solutions. The relative magnitudes of the above 2 expressions, on which depends the direction of displacement, can be affected in 2 ways, with the possibility of reversing them entirely. First, the values of p_+ and p_- can be changed at will, by regulating the ionic concentrations and, second, the values of P_+ and P_- can be altered by substituting solutions of the metals in mercury for the metals themselves.

To take a concrete example, it appears very probable, from the results obtained, that finely divided barium could be made to precipitate potassium from a saturated solution of its hydroxide or carbonate, if it were not for the action of the displaced potassium, not to mention the barium, on the water of the solution. On providing for a lower solution pressure of the displaced potassium, however, by the substitution of barium amalgam for free barium, whereby the solution pressure of the barium is also lowered, the action of the water is greatly retarded, and the precipitation of potassium from certain of its salt solutions by barium may be accomplished readily.

In the case of barium amalgam and potassium chloride

solution (Exp. 11), only a trace of potassium entered the amalgam. This was due, in part, to the fact that the barium which entered the solution remained dissolved, and also that the amalgamated metals, owing to the presence of hydrogen ions in the solution, were enabled to enter the solution by virtue of their action on the water. On reducing the ionic concentration of the barium to a minimum, by the substitution of a saturated solution of potassium sulphate in place of the chloride solution, many times the amount of potassium entered the amalgam (Exp. 12); but the actual quantity was in this case also very small. When, however, a high concentration of potassium ions was provided for and, at the same time, the ionic concentration of both barium and hydrogen were kept at a minimum, it was found that potassium readily entered the amalgam. These conditions were realized by the employment of a concentrated solution of potassium hydroxide, or carbonate (Exps. 13-14). The solubility product of the barium hydroxide, or carbonate formed was immediately exceeded in the corresponding solution and, owing to the hydroxyl ions present, the ionic concentration of hydrogen was so low in each case that no perceptible evolution of gas took place.

In this connection, it is interesting to compare the action of barium and strontium amalgams on saturated solutions of potassium and sodium chlorides and sulphates. While barium amalgam displaces the metals from these solutions only with great difficulty, they are readily displaced from the solutions by strontium amalgam. In other words, the values of the solution pressures of the alkali earth metals in these amalgams are of an inverse order as compared with those of the metals themselves. The same behavior is repeated by strontium and calcium in the action of their amalgams on lithium salt solutions.

Besides having confirmed certain consequences of Nernst's theory of electrolytic solution pressures, the results of this investigation have led to the solution of another important question, *viz.*, the nature of solutions of the metals of the alkali and alkali earth groups in mercury.

Assuming that these metals exist in dilute solution in the form of monatomic molecules, let us consider the case of equimolecular solutions of them in mercury. Under this assumption, we should expect the solution pressures of the dissolved metals to be similarly affected; they should all be correspondingly lowered, and the electromotive series should still read,

+K, Na, Li, Ba, Sr, Ca, Mg—.

However, it is apparent from the results obtained that such is no longer the case. In so far as can be judged from these results, the series reads,

+Mg, Li, Ca, K, Na, Sr, Ba—.

This irregular alteration of the solution pressures of the dissolved metals can only be accounted for by the assumption that, with the possible exception of magnesium, compounds of the metals and mercury exist, even in very dilute solution.

It may be added, however, that the solution pressures exerted by the alkali and alkali earth metals in these amalgams are possibly due to a partial dissociation of the compounds in solution. In the case of a relatively stable amalgam, like that of barium, this dissociation is evidently very slight, while in that of an unstable amalgam, *e. g.*, calcium amalgam, it is relatively greater.

SUMMARY.

It has been experimentally shown in the present investigation:

1. That the following 16 pairs of metals are reversibly displaceable in aqueous solutions: K–Na, K–Li, K–Ba, K–Sr, K–Ca, K–Mg; Na–Li, Na–Ba, Na–Sr, Na–Ca, Na–Mg; Li–Sr, Li–Ca; Ba–Mg; Sr-Ca, Sr–Mg.

2. That in the presence of mercury, lithium can be displaced from a mixed solution of its chloride and hydroxide by magnesium, with the formation of lithium amalgam. In like manner, barium can be displaced from its chloride solution by the amalgams of the more electronegative metals, strontium and calcium.

3. That, contrary to the generally accepted view, the metals

of the alkali and alkali earth groups, with the possible exception of magnesium, do not exist as such, in solution in mercury, in the form of monatomic molecules. The liquid amalgams of these metals are solutions in mercury of compounds of the general formula MHg_m, containing only 1 atom of the amalgamated metal to the molecule.

4. That the stability of these compounds increases in the following order: $LiHg_m$, KHg_m, $NaHg_m$, for the alkali compounds; and $CaHg_m$, $SrHg_m$, $BaHg_m$, for those of the alkali earths.

5. That the same equilibrium is obtained by the action of an equimolecular solution of sodium and potassium chlorides on either potassium, sodium, or lithium amalgam.

URBANA, ILLINOIS,
December 20, 1906.

OBITUARY.

MARCELLIN PIERRE EUGÈNE BERTHELOT.

Professor Berthelot was born in Paris, October 25, 1827, and died in the same city, from heart failure, a few hours after the death of his wife, March 18, 1907. Like Moissan, the whole of Berthelot's active life was spent in Paris. He received the Doctor degree from the University in 1854, was "Préparateur" in the Collège de France, 1859–76. In 1860 he became professor of organic chemistry at the Ecole de Pharmacie and in 1865 a chair of theoretical chemistry was created for him in the Collège de France.

It is impossible to give, in a brief space, any adequate account of Berthelot's investigations; his original papers are numbered by the hundreds and include contributions to every branch of chemical science. In organic chemistry he is, perhaps, best known for his investigations into the nature of fats, for his synthetic work and his contributions to our knowledge of the terpenes. Although, of course, he did not discover acetylene, yet everything of importance that we know of its properties is due to his investigations. Analytical chemistry has also benefited by his labors. In the domain of explosives he was second to none, and it is due essentially to his work that France became equipped with smokeless powder. To Berthelot we owe an enormous quantity of thermo-chemical data and it is because of his supreme influence that French In-

organic Chemistry is essentially "thermic" and not "ionic."[1] His physical-chemical work extended much further, however, and included numerous investigations in electro-chemistry, the action of light, etc. Berthelot contributed largely to extending our knowledge of the chemistry of plants and animals, including the chemical activity of bacteria. In short, it may be said with truth that his contributions to any one branch of chemistry were each sufficient to earn for him no small measure of fame—how much more is due, therefore, for his contributions to all regions of the science?

Berthelot's activities were by no means confined to the laboratory, he was the author of numerous text-books and of many essays, reports, pamphlets, etc. Special mention must be made of his volumes on ancient alloys. His political activities are shown by his being Minister of Education, 1886–87, and Minister of Foreign Affairs, 1895-96. It is hardly necessary to add that he was a member of practically every government commission which had any connection with science. That his native country appreciated him is shown by his becoming a life Senator in 1881. He has been Secretary of the French Academy since 1889. In 1876 he was appointed Inspector-General of Higher Education.

Berthelot was a Foreign Associate of the National Academy of Sciences, a member of the American Philosophical Society, Honorary Member of the German and American Chemical Societies and a Foreign Member of the Chemical Society (London). He was elected a Foreign Member of the Royal Society in 1877 and subsequently received from it the Copley and Davy medals. In 1901 Berthelot received an international "medal of honor," in recognition of his position among French chemists and of his services to the science.

REPORT.

The Alkylation of Metallic Cyanides.

In a recent paper Guillemard[2] describes the results obtained when metallic cyanides are treated with alkyl oxides and methyl sulphates under varying conditions of temperature and for different periods of time. The amounts of cyanide and isocyanide formed are a function of the temperature and time, because the isocyanide, which is produced at low temperatures, is changed over to the more stable cyanide by continued heating at a higher temperature. The cyanides of potassium,

[1] Cf. THIS JOURNAL, 35, 470.
[2] Compt. rend., 144, 326.

silver, zinc, nickel, copper and mercury, the ferrocyanides of potassuim, lead and silver, and the ferricyanides of potassium and silver were used in the experiments. With potassium cyanide and ethyl iodide only the cyanide could be isolated, because the isocyanide which was first formed combined with the ethyl iodide. When the silver cyanide was used and the mixture was kept at 80°, for 4 hours, only isocyanide was obtained. If, however, the action was carried on at a higher temperature, for a longer time, a mixture of cyanide and isocyanide was produced, the quantity of isocyanide decreasing with rise in temperature. Nickel cyanide yielded only isocyanide below 140°, but above this temperature a mixture of cyanide and isocyanide. The conclusion, from a number of experiments, was that at low temperatures only the isocyanide was formed, at higher temperatures a mixture, and about certain temperatures only the cyanide. The author accepts the view advanced by Nef, that at ordinary temperatures all metallic cyanides should be represented by the formula MNC. He regards the formation of cyanides at high temperatures as due to a rearrangement of the isocyanide to form the more stable cyanide, this change being accompanied by evolution of heat. He gives, as an example of such a change, the formation of benzonitrile from diphenylthiourea or from formanilide. J. E. G.

REVIEWS.

A History of Chemical Theories and Laws. By M. M. Pattison Muir, M.A., Fellow and Prœlector in Chemistry of Gonville and Caius College, Cambridge. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1907. 8vo. pp. xx + 555. Price, Cloth, $4.00 net.

In his preface the author says: "I have not attempted the uncalled-for task of writing a history of chemistry. To do that, at present, would be to produce a mighty volume, containing a series of text-books, a bewildering catalogue of facts, a sheaf of biographical essays, supplemented by prolegomena, appendices, and chronological tables.

"The object of this book is to set forth what seemed to me the main lines along which the science of chemistry has advanced to its present position. In making an attempt to do this in an orderly fashion, with some fulness of detail, and, I hope, some sense of proportion, I have passed over very many able memoirs; I have not mentioned the chemical histories of particular substances, except in so far as these have appeared to me to illustrate the development of some law, theory, or hy-

pothesis of general importance. I describe only those investigations which, in my judgment, have given powerful impulses to the advance of chemical science along paths already trodden, or have opened new ways of progress."

In his introduction he says: "The subject proper of this book will be dealt with broadly as follows:

"I. The history of the attempts to answer the question, What is a homogeneous substance?

The recognition of homogeneous substances, and the description of chemical changes as interactions of these substances;
The marks of elements and of compounds;
The laws of chemical combination, the atomic hypothesis, the molecular and atomic theory;
The more searching examination of the compositions of homogeneous substances, allotropy;
Elements which do not react;
Chemical nomenclature and notation.

"II. The history of the attempts to answer the question, What happens when homogeneous substances interact?

The classification of homogeneous substances;
Acids, bases, salts;
Radicals, types, dualism, the unitary hypothesis;
Chemical equivalency;
Isomerism and constitutional formulae;
Application of the hypothesis of ionization to the classification of homogeneous substances;
The conditions and general laws of chemical change;
Chemical affinity;
Chemical equilibrium;
The elucidation of chemical reaction by measurements of physical properties."

This book can be conscientiously recommended to all chemists. It will repay a careful study, whether the chemist be old or young, provided he is interested in the history of the development of his science. It has the great advantage of being readable. The author has shown much skill in selecting material for treatment. By throwing emphasis upon the essentials he avoids confusion by passing over those things which, however interesting from some points of view, are not essential to the development of chemistry.

In the first chapter he gives a sketch of the progress of chemical conceptions from early times to the discovery of oxygen. Of course, this is a sketch. His first sentence is interesting. It is this: "Chemistry is a universal science; it was founded

by many whose memories are forgotten. The foundations of chemistry are laid deep in the experiences, in the hopes, the visions of mankind."

This is evidently suggested by the narrower statement of Würtz, which provoked so much adverse criticism nearly 40 years ago: "La chimie est une science française; elle est constitué par Lavoisier d'immortelle mémoire."

The principal results of the experiments of Priestley, Scheele, Lavoisier, Boyle, Cavendish, are well summarized in this chapter, which ends in these words: "It is not often that the power of destroying and the power of reconstructing are united in so extraordinary a degree as they were united in Lavoisier, the greatest of all chemists."

In the next chapter the work of Lavoisier is more fully and very clearly treated. Dalton's writings are skilfully and most satisfactorily presented. In regard to the atomic theory the author says: "Notwithstanding its incompleteness, Dalton's atomic theory is an immense help to the solution of the two fundamental questions of chemistry; indeed it would not be an exaggeration to say that the most important advances made in chemistry since the publication of the "*New System*" have been made by following lines of research suggested by applications of the atomic theory."

In a later chapter, which has to deal with elementary substances, the author again returns to Lavoisier, referring to him in these words: "Before the close of the alchemical period we find several exact students of nature who had gained fairly clear conceptions of composition; the most notable of these was Boyle."

"The preparation had been long and varied; suddenly, it seems to us, as we look back, chemistry began, fashioned from the materials which the centuries had gathered, by a man of supreme genius. Lavoisier was dowered by nature with the power of thinking accurately, and, as we say, scientifically. He did not free himself from the trammels of the phlogisteans; he was free-born."

Although the author disclaims any intention of writing "a history, either of physical chemistry or of chemical physics," he has succeeeded in presenting those features of this subject which are of most interest to what may distinctively be called chemistry, and even one who has not attempted to follow all the advances of physical chemistry would be able to see the bearings of the advances in this field on the progress of chemistry. But in this notice it is impossible to go into further details. Only by studying the book can any one form an ade-

quate conception of it. It is well worth the study, and should take its place in the library of every earnest chemist. I. R.

A TEXT-BOOK OF ELEMENTARY ANALYTICAL CHEMISTRY, QUALITATIVE AND VOLUMETRIC. By JOHN H. LONG, M.S., Sc.D., Professor of Chemistry and Director of the Chemical Laboratories in the Northwestern University Medical School. Third edition, revised and enlarged. Philadelphia: P. Blakiston's Son & Co. 1906. Price, $1.25 net.

The author states in the preface that, in this edition, several important additions have been made. Besides minor changes throughout the book, there has been added a chapter discussing reactions in solutions, in which such matters as chemical equilibrium, solubility product, hydrolysis, oxidation and reduction are included.

After treating the matter of qualitative analysis in the way found in most text-books on this subject, the author discusses the reactions of a few organic substances and the methods to be followed in the examination of poisons. In the portion devoted to quantitative analysis typical examples of the different varieties of quantitative methods, both volumetric and gravimetric, and the methods used in the analysis of water and some other common substances are given.

This book could be used to advantage with students who are only required to study chemistry for 2 years and wish, during this time, to get some knowledge of quantitative work in addition to the qualitative methods which are almost always studied in the second year. For medical students, for whom no doubt the volume is intended, the course here given would be well suited, provided the introduction of the quantitative work did not prevent them from taking a course in organic chemistry. J. E. G.

MONOGRAPHIEN ÜBER ANGEWANDTE ELEKTROCHEMIE. XXIV Band. Die Elektrochemischen Deutschen Reichspatente. Auszüge aus den Patentschriften gesammelt, geordnet und mit Hinweisen versehen von DR. P. FERCHLAND und DR. P. REHLÄNDER. Mit 124 Figuren im Text. Halle a. S.: Wilhelm Knapp. 1906. pp. 230. Price, M. 10.

This monograph is the result of much labor and skill expended in classifying, excerpting and criticizing the German patents. The list is complete to May, 1906.

The first section—inorganic—includes all patents for electrolytic production of the light metals, alkalis, halogens, bleaching liquids, oxidized salts (permanganates, percarbonates, etc.), barium and strontium hydroxides, carbides, ozone, nitrogen compounds, and the heavy metals and their derivatives. The section on organic work includes patents for making aniline, benzidine, paraminophenol, dyestuffs and pharmaceutical

products. This is a valuable book of reference for chemists. E. R.

OUTLINES OF QUALITATIVE CHEMICAL ANALYSIS. By FRANK AUSTIN GOOCH, Professor of Chemistry in Yale University, and PHILIP EMBURY BROWNING, Assistant Professor of Chemistry in Yale University. First edition. New York: John Wiley & Sons. pp. 145. Price, $1.25 net.

This book is very elementary. The tabular method used in most manuals to show the separations of the ions in a given group is here also used to show the behavior of the ions toward reagents. The equations for all reactions used in separations are printed in full. The methods are, in the main, the common ones. E. R.

CONTRIBUTION A L'ÉTUDE DE LA SAPONIFICATION DES CORPS GRAS. Par M. MAURICE NICLOUX, Docteur ès Sciences, Docteur en Médecine, chef de Laboratoire a la Faculté de Médecine, Lauréat de l'Institut. etc. Paris: Librairie Scientifique, A. Hermann. 1906. pp. 76. Price, 3 Fr.

This monograph is devoted to an account of the author's researches on the fat hydrolyzing substance in the seeds of the castor oil plant. It is divided into 7 sections dealing, at some length, with the extraction of the active material and its lipolytic and hydrolytic powers under various conditions. The most important conclusion which is drawn is that the lipolytic activity is not due to a soluble diastatic ferment, but is inherent in the cytoplasm itself. This result is not in harmony with the conclusions of other workers in the same field.

J. B. T.